Roles of Nano- and Micro-Scale Subsurface Geochemical Reactions on Environmentally Sustainable Geologic CO2 Sequestration

Yandi Hu

Follow this and additional works at: http://openscholarship.wustl.edu/etd

Recommended Citation
http://openscholarship.wustl.edu/etd/1136
WASHINGTON UNIVERSITY IN ST. LOUIS

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

Dissertation Examination Committee:

Young-Shin Jun, Chair
Daniel Giammar
Cynthia Lo
Palghat Ramachandran
Phil Skemer
Carl Steefel

Roles of Nano- and Micro-Scale Subsurface Geochemical Reactions on Environmentally Sustainable Geologic CO₂ Sequestration

by
Yandi Hu

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

August 2013
Saint Louis, Missouri
# Table of Contents

Acknowledgments ........................................................................................................ vi

ABSTRACT OF THE DISSERTATION ........................................................................ viii

Chapter 1. Introduction ................................................................................................ 1

1.1 Background .......................................................................................................... 1

1.1.1 Geologic CO₂ Sequestration (GCS) ................................................................. 1

1.1.2 Relevant GCS Conditions regarding Temperature, Pressure, Brine, and Rock Compositions .......................................................................................................... 2

1.1.3 Effects of CO₂-Brine-Rock Interactions on GCS ................................................. 5

1.2 Research Objectives and Tasks ........................................................................... 7

1.2.1 Limitations of Previous Studies and General Scopes of Current Studies .......... 7

1.2.2 Specific Research Objectives ......................................................................... 9

1.3 Dissertation Overview ......................................................................................... 11

Chapter 2. Biotite–Brine Interactions: Fibrous Illite, Goethite, and Kaolinite Formation and Biotite Surface Cracking ............................................................. 15

Abstract .................................................................................................................... 15

2.1 Introduction ......................................................................................................... 16

2.2. Experimental Section ...................................................................................... 17

2.2.1 Minerals ......................................................................................................... 17

2.2.2 High Pressure and Temperature Reaction ...................................................... 17

2.2.3 Identification of Secondary Mineral Phases ................................................... 19

2.3. Results and Discussion .................................................................................... 20

2.3.1 Fibrous Precipitate Formation on Flat Biotite Basal Planes ......................... 22

2.3.2 Cracking and Detachment of Biotite Basal Surface Layers and Detachment of Fibrous Illite ........................................................................................................ 25

2.3.3 Preferential Al-Substituted Goethite and Kaolinite Precipitation on Biotite Edge Surfaces ........................................................................................................... 28

2.3.4 Aqueous Chemistry Evolution and Linkages with Solid Alterations .............. 29

Supporting Information for Chapter 2 .................................................................... 34

Chapter 3. Na⁺, Ca²⁺, and Mg²⁺ in Brines Affect CO₂–Brine–Biotite Interactions ....... 63

Abstract .................................................................................................................... 63
3.1 Introduction .................................................................................................................. 64
3.2 Experimental Section .................................................................................................. 65
  3.2.1 Chemicals and Minerals ........................................................................................ 65
  3.2.2 High Pressure/Temperature Experiments, Analytical Methods, and Thermodynamic
      Calculations .............................................................................................................. 66
3.3 Results and Discussion ............................................................................................... 67
  3.3.1 Ion Exchange Reactions and K⁺ Release from Biotite ........................................ 67
  3.3.2 Morphological Evolutions of Biotite Basal Surfaces and Relevance to Ion Exchange
      Reactions ..................................................................................................................... 70
  3.3.3 Release of Biotite Framework Ions and Its Relevance to Ion Exchange Reactions and
      Morphological Changes ............................................................................................... 72
  3.3.4 Fibrous Illite Precipitation and Its Detachment from the Surface ....................... 73
  3.3.5 Enhanced Biotite Dissolution and Morphological Evolution by CO₂ Injection ...... 77
3.4 Environmental Implications ....................................................................................... 77
Supporting Information for Chapter 3 ........................................................................... 79

Chapter 4. Biotite Dissolution in Brine: Its Activation Energy and CO₂ Intercalation ...... 91
Abstract ......................................................................................................................... 91
4.1 Introduction ................................................................................................................. 93
4.2 Experimental Section .................................................................................................. 95
  4.2.1 Chemicals and Minerals ...................................................................................... 95
  4.2.2 High Pressure/Temperature Experimental Design and Setups, Analytical Methods, and
      Thermodynamic Calculations .................................................................................... 95
4.3 Results and Discussion ............................................................................................... 97
  4.3.1 Effects of Temperature on Biotite Surface Cracking and Dissolution Congruency:
      Calculations of Dissolution Activation Energy .......................................................... 97
  4.3.2 Differentiation of the pH Effects of CO₂ from the Effects of Bicarbonate
      Complexation and CO₂ Intercalation ......................................................................... 101
  4.3.3 CO₂–Brine–Biotite Interactions at Varied CO₂ Pressures Relevant to GCS .......... 107
4.4 Conclusions ............................................................................................................... 110
Supporting Information for Chapter 4 ........................................................................... 112

Chapter 5. Environmentally Abundant Anions Influence the Nucleation, Growth, Ostwald
Ripening, and Aggregation of Hydrous Fe(III) Oxides .................................................. 122
Abstract ......................................................................................................................... 122
5.1 Introduction .................................................................................................................. 123

5. 2. Experimental Section .................................................................................................. 126

5.2.1 Substrate and Solution Preparation ......................................................................... 126

5.2.2 In Situ SAXS/GISAXS Measurements .................................................................... 127

5.2.3 Analysis of SAXS/GISAXS Scattering Data and Calculation of Total Volume, Size, Number, and Surface Area of the Primary Particles .................................................. 128

5.2.4 Zeta Potential (ζ), Hydrodynamic Particle Size, and Atomic Force Microscopy (AFM) Measurements ........................................................................................................... 129

5.2.5 Precipitate Phase Identification .............................................................................. 130

5.3. Results and Discussion ................................................................................................ 131

5.3.1 Sizes of the Particles Precipitated on the Quartz Surface and in Solution .......... 131

5.3.2 Volumes of the Particles Precipitated on the Quartz Surface and in Solution ........ 136

5.3.3 Nucleation, Growth, Ostwald Ripening, and Aggregation Processes during Hydrous Fe(III) Oxide Precipitation ...................................................................................... 142

5.4. Conclusions and Implications ...................................................................................... 147

Supporting Information for Chapter 5 ................................................................................ 149

Chapter 6. Control of Heterogeneous Fe(III) (Hydr)oxide Nucleation and Growth on Quartz, Mica, and Sapphire by Interfacial Energies and Local Saturations ......................................... 160

Abstract ............................................................................................................................. 160

6.1 Introduction ..................................................................................................................... 161

6.2. Materials and Methods ............................................................................................... 163

6.2.1 Substrate and Solution Preparation ......................................................................... 163

6.2.2 In Situ GISAXS Measurements .............................................................................. 164

6.2.3 GISAXS Data Analysis ........................................................................................... 165

6.2.4 Atomic Force Microscopy, Zeta Potential (ζ), and Contact Angle Measurements .... 166

6.2.5 Precipitate Phase Identification .............................................................................. 167

6.3. Results .......................................................................................................................... 167

6.3.1. Size and Relative Total Volume Quantification of the Precipitates on Substrates ... 167

6.3.2. Surface Charges of the Precipitates and the Substrates ........................................ 170

6.3.3. Water Contact Angles on Substrates and Their Relation to Substrate–Water Interfacial Energies ................................................................................................................ 172

6.4. Discussion .................................................................................................................... 173
6.4.1. Defining the Nucleation and Growth Rates during Fe(III) (hydr)oxide Precipitation ................................................................. 173
6.4.2. Comparatively Slow Heterogeneous Growth on Sapphire: Role of Electrostatic Forces ................................................................. 174
6.4.3. The Comparatively Fast Heterogeneous Nucleation on Sapphire: Role of Interfacial Energies .......................................................... 176

6.5. Environmental Implications .................................................................................................................................................. 178

Supporting Information for Chapter 6 ............................................................................................................................................... 180

Chapter 7. Conclusions and Future Directions ............................................................................................................................. 191
7.1 Conclusions ................................................................................................................................................................................. 191
7.2 Recommended Future Directions ........................................................................................................................................... 193

Appendix A. In situ Determination of Interfacial Energies between Heterogeneously Nucleated CaCO₃ and Quartz Substrates: Thermodynamics of CO₂ Mineral Trapping . 197
Abstract ........................................................................................................................................................................................ 197
A.1. Introduction ........................................................................................................................................................................... 198
A.2. Experimental Section .............................................................................................................................................................. 201
A.3. Results and Discussion ............................................................................................................................................................ 205

Supporting Information for Appendix A .......................................................................................................................................... 217

Appendix B. Viability and Metal Reduction of Shewanella Oneidensis MR-1 under CO₂ Stress: Implications for Ecological Effects of CO₂ Leakage from Geologic CO₂ Sequestration ........................................................................................................ 227
Abstract ........................................................................................................................................................................................ 227
B.1. Introduction ........................................................................................................................................................................... 228

B.2. Materials and Methods ........................................................................................................................................................... 231
B.2.1. Reactor setup and experimental conditions .......................................................................................................................... 231
B.2.2. Microorganism cultivation .................................................................................................................................................. 231
B.2.3. Measurement of extracellular polymeric substances (EPS) and membrane integrity .......................................................... 232
B.2.4. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) observations of microbial cells .......................................................... 233
B.2.5. Measurements of Ca²⁺ release from calcite coupons, lactate consumption ................................................................. 234
B.2.6. MnO₂ reduction capability measurements .......................................................................................................................... 234

B.3. Results and Discussion ........................................................................................................................................................... 235
B.3.1 Cell viability under CO₂ stress................................................................. 235
B.3.2 Alleviation of CO₂ stress under environmental conditions...................... 239
B.3.3 MnO₂ reduction by stressed cells............................................................. 241
B.3.4 Modeling bacterial viability under CO₂ stress............................................. 242

B.4. Environmental Implications......................................................................... 243

Supporting Information for Appendix B........................................................... 246

Appendix C. Curriculum Vitae ............................................................................. 252

References............................................................................................................ 256
Acknowledgments

I would like to express my greatest appreciation to my advisor Dr. Young-Shin Jun for her tremendous support and advice, leading me into the field of environmental geochemistry and environmental nanochemistry, and turning me from a graduate student into an independent researcher.

I would like to thank Drs. Daniel Giammar, Cynthia Lo, Palghat Ramachandran, Phil Skemer, and Carl Steefel for kindly serving on my thesis committees, and giving their valuable time and precious suggestions in helping improve my research. I am very grateful for Dr. Carl Steefel’s support and guidance in using reactive transport modeling and his continuous advice and encouragement through my graduate study. I am also grateful to Dr. Daniel Giammar’s valuable insights. I would also like to express my gratitude to my collaborators, Drs. Alejandro Fernandez-Martinez and Glenn A. Waychunas at Lawrence Berkeley National Lab (LBNL) in the calcium carbonate nucleation research, and Drs. Byeongdu Lee and Soenke Seifert at Argonne National Lab (ANL), for their valuable insights on X-ray scattering techniques. I would also like to give my thanks to Prof. James Ballard for helping me to improve my writing.

I would also like to acknowledge the former and current members of the Environmental Nanochemistry Laboratory. I sincerely thank Dr. Hongbo Shao, who served as a mentor when I started to work in the lab. I am also very grateful to Dr. Debin Wang, Jessica Ray, Chelsea Neil, and Qingyun Li for their assistance in conducting parts of the experiments. Discussions with Yi Yang always inspired me. Special thanks are extended to other colleagues and friends in the department of Energy, Environmental & Chemical Engineering for making my PhD life colorful and enjoyable.
Financial support from the Consortium for Clean Coal Utilization, Washington University’s Faculty Start up Grant, the Department of Energy (DOE)’s Energy Frontier Research Center (EFRC), and the National Science Foundation (NSF) is gratefully acknowledged.

Last but the most important, I wish to give my biggest thanks to my parents and parents in-law for their unreserved support and endless love. I have also been lucky to meet Yang Liu and marry him: he always brings sunshine into my life when I am in the dark. I would also like to thank my lovely daughter, Emily, whose smile inspired me in my research. The responsibility of taking care of her made me stronger mentally to conquer the difficulties in research and life.

Yandi Hu

Washington University in St. Louis

May 2013
ABSTRACT OF THE DISSERTATION

Roles of Nano- and Micro-Scale Subsurface Geochemical Reactions on Environmentally Sustainable Geologic CO₂ Sequestration

by

Yandi Hu

Doctor of Philosophy in Energy, Environmental, and Chemical Engineering

Washington University in St. Louis, 2013

Professor Young-Shin Jun, Chair

Geologic CO₂ sequestration (GCS) is a promising approach to reduce anthropogenic CO₂ emissions into the atmosphere. At GCS sites, injected CO₂ is kept in formation rock by an overlying low permeability caprock. During and after CO₂ injection, geochemical reactions can affect the porosity, permeability, and pollutant transport in aquifers. Despite their importance, nano- and micro-scale subsurface geochemical reactions are far from well-understood.

Clay mobilization has been reported to decrease aquifer permeability during water flooding, and clay minerals are abundant in caprock. Thus, we studied CO₂-brine-clay interactions under varied conditions relevant to different GCS sites (at 35-95°C and under 35-120 atm CO₂, in water, NaCl, MgCl₂, or CaCl₂ solutions). Biotite, Fe-bearing mica, was used as a model clay mineral. We observed numerous fibrous illite precipitates on mica after reaction for only 3 h, which had not been previously reported. A few hours later, the mica surface cracked and fibrous illite detached. The mobilization of fibrous illite can decrease the aquifer’s
permeability greatly and affect the safety and efficiency of GCS. Mechanisms related to ion exchange, mica swelling, and CO$_2$ intercalation were explored. Oriented aggregation of illite nanoparticles forming the fibrous illite was directly observed, suggesting a new mechanism for fibrous illite formation. Interestingly, besides the pH effect, aqueous CO$_2$ enhances mica cracking over N$_2$. These findings can help to achieve safer subsurface operations.

At GCS field sites, Fe concentration increased near the injection sites and originally adsorbed pollutants were released. As the brine flows, Fe re-precipitated because of pH increase. To better predict the fate and transport of aqueous pollutants, the nucleation and growth of Fe(III) (hydr)oxides were studied. New information about sizes and volumes of the Fe(III) (hydr)oxide nanoparticles precipitated in solution and on quartz, mica, and sapphire were provided using small angle X-ray scattering, in the presence of different ions (Al$^{3+}$, Cl$^-$, NO$_3$ and SO$_4^{2-}$). Using complementary techniques, the controlling mechanisms related to surface charge, bond formation, and interfacial energies were explored. These new findings can help better predict pollutant transport in aquifers not only at GCS sites, but also in managed aquifer recharge and acid mine drainage sites.
Chapter 1. Introduction

1.1 Background

1.1.1 Geologic CO₂ Sequestration (GCS)

Long-term geologic CO₂ sequestration (GCS) in deep saline aquifers is one of the most promising options for decreasing atmospheric CO₂ concentration\(^1\) and alleviating the global climate-change problems caused by the substantial increase in emissions of carbon dioxide and other greenhouse gases into the atmosphere. At GCS sites, CO₂ is injected into a formation (generally sandstone) with relatively high porosity and permeability, where the CO₂ migrates through the porous media from the injection site and is stored in the pores.

\[\text{Figure 1.1 Four trapping mechanisms of CO}_2\text{.}^2\]
After injection, there is a tendency for CO$_2$ to escape by migrating upward due to buoyant force. To prevent CO$_2$ leakage, a caprock (generally claystone layers) with low porosity and permeability is required above the storage formation (Figure 1.1A). The caprock traps the CO$_2$ right after injection, in a process called structural trapping. After injection, the supercritical CO$_2$ will move through the porous rock and displace brine. As the CO$_2$ continues to move, fluid will again replace it, and some of the CO$_2$ will be left behind as disconnected—or residual—droplets in the pore spaces, which are immobile (Figure 1.1B; residual trapping or capillary trapping). When CO$_2$ contacts with the brine in the porous rock, it will dissolve in the brine. The brine containing CO$_2$ is denser than the surrounding fluids and thus sinks (Figure 1.1C). This trapping mechanism can trap CO$_2$ more securely (solubility trapping). As time goes on, the formation of carbonic acid will cause mineral dissolution, and the dissolved cations can form carbonate minerals such as siderite, dolomite, and calcite (Figure 1.1D). This final stage is called mineral trapping.

1.1.2 Relevant GCS Conditions regarding Temperature, Pressure, Brine, and Rock Compositions

The phase diagram of CO$_2$ is shown in Figure 1.2. The critical point for CO$_2$ to be in the supercritical phase is 31 °C and 73 atm. At GCS sites, the injection depth of CO$_2$ could vary greatly. With increasing depth, the temperature and pressure increase accordingly. In general, the
injection depth should be deeper than 800 m, where the high temperature and high pressure allow CO₂ to be in the supercritical phase. If the injection depth is too shallow, the temperature and pressure are low, thus CO₂ would be in the gas phase. The density of supercritical CO₂ is much larger than that of gas phase CO₂, so the total mass of CO₂ stored in a reservoir with fixed pore volume will be much less. However, if the injection depth is too deep, more energy will be consumed to drill the well and pump CO₂ in.

![Phase diagram of CO₂](image)

**Figure 1.2. Phase diagram of CO₂.**

In deep saline aquifers used for CO₂ storage, the temperature range encountered is 31 °C ≤ T ≤ 110°, and the pressure range is 72.8 < P ≤ 592 atm. For example, EnCana's CO₂ injection EOR (Enhancing Oil Recovery) project at Weyburn (Saskatchewan, Canada) is the most
important oil production development that hosts an international monitoring project. The injection depth is around 1300–1500 m, and the pressure and temperature of the reservoir are 15 MPa (150 atm) and 62 °C, respectively.\(^7\) At the Frio-I Brine Pilot test site, the injection depth is 1541–1546 m, with a pressure of about 152 bar and a temperature of about 59 °C.\(^6\)

As shown in Table 1.1, an Indiana geologic survey found that the brine in deep saline aquifers is highly saline. There are especially high concentrations of NaCl \((0.01 \leq \text{NaCl} \leq 2 \text{ M})\),\(^8\) and there can also be high concentrations of Mg \((0–0.1 \text{ M})\) and Ca \((0–0.2 \text{ M})\). As shown in Table 1.1, the pH values of the brine in deep saline aquifers are generally neutral without CO\(_2\) injection. After CO\(_2\) injection, the pH variations at GCS sites are a function of both the distance from the injection sites and the time after injection. Near the injection site, the pH could be around 3–6.\(^9\)

**Table 1.1.** Brine compositions in deep saline aquifers in the Indiana geologic survey.\(^8\)

<table>
<thead>
<tr>
<th>Cations</th>
<th>Na (M)</th>
<th>Ca (M)</th>
<th>Mg (M)</th>
<th>Total Fe (mM)</th>
<th>K (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>0.01–2</td>
<td>0–0.2</td>
<td>0–0.1</td>
<td>0–21</td>
<td>0–21</td>
</tr>
<tr>
<td>General range</td>
<td>0.04–1.2 M</td>
<td>0.01–0.1</td>
<td>0.02–0.05</td>
<td>0.2–1.8</td>
<td>0.9–3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anions and pH</th>
<th>Cl (M)</th>
<th>SO(_4) (M)</th>
<th>HCO(_3) (mM)</th>
<th>Br (mM)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>0.01–3.3</td>
<td>0–0.06</td>
<td>0–27</td>
<td>0–2.5</td>
<td>1.25–11.5</td>
</tr>
<tr>
<td>General range</td>
<td>0.3–2.2 M</td>
<td>0.01–0.05</td>
<td>2–10</td>
<td>0.6–1.9</td>
<td>6.5–8.2</td>
</tr>
</tbody>
</table>

The mineralogical compositions of the rocks can vary greatly at different field sites. Generally, caprock contains mainly clay minerals, including mica, illite, and kaolinite, as well as quartz and carbonate.\(^7,9,10\) Formation rock contains mainly feldspar, quartz, carbonate, and clay
minerals. For example, at a depleted on-shore gas reservoir in Northern Italy (Table 1.2), the caprock is composed of carbonate-rich shales (33 v/v %) and silicate clay minerals (47 v/v %, including muscovite, Na-smectite, chlorite, kaolinite, and illite) and non-clay silicates represented by quartz (20 v/v%). For the reservoir formations, non-clay silicates (53 v/v%, including quartz, K-feldspar, and albite) are the main components. There is also significant amount of carbonate (16 v/v%) and clay minerals (31 v/v%, including muscovite, chlorite, kaolinite, illite, and Na-smectite).

Table 1.2. Mineral compositions (volume percentage) in caprock and formation rocks.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Caprock</th>
<th>Reservoir formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>0.30 ± 0.10</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.03 ± 0.02</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.20 ± 0.05</td>
<td>0.35 ± 0.02</td>
</tr>
<tr>
<td>Illite</td>
<td>0.03 ± 0.01</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>0</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.06 ± 0.02</td>
<td>0.09 ± 0.03</td>
</tr>
<tr>
<td>Albite</td>
<td>0</td>
<td>0.15 ± 0.03</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.04 ± 0.02</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td>Na-smectite</td>
<td>0.15 ± 0.05</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>Muscovite</td>
<td>0.20 ± 0.05</td>
<td>0.15 ± 0.05</td>
</tr>
</tbody>
</table>

1.1.3 Effects of CO₂-Brine-Rock Interactions on GCS
During and after CO₂ injection, CO₂–brine–rock interactions can promote significant geochemical reactions, which can alter the brine composition and cause porosity, permeability, reactivity, and wettability changes of the caprock and formation rock. Lowering the porosity and permeability of the storage formation will lower its injectivity and reduce its storage capacity, while increasing the porosity and permeability of the caprock might lead to potential CO₂ leakage. Changes in wettability will affect the capillary pressure at GCS sites. All of these changes will influence the seal integrity and CO₂ injectivity, which are essential for safer and more efficient GCS. Also, CO₂–brine–rock interactions may cause the release of aqueous pollutants, which can be transported with the flow of the brine driven by CO₂ injection. In order to better understand the fate and transport of the aqueous pollutants released by CO₂ injection, a more comprehensive understanding of CO₂-brine-rock interactions under GCS conditions is imperative.
1.2 Research Objectives and Tasks

1.2.1 Limitations of Previous Studies and General Scopes of Current Studies

For CO$_2$–brine–rock interactions under GCS conditions, extensive studies have been done on feldspar$^{12, 13}$ and carbonate$^{14, 15}$ because of their abundance and fast dissolution rates. However, under GCS conditions, the behavior of clay minerals has been much less studied, although they are a major component of caprock at GCS sites.$^{16-18}$

In particular, at field sites, clay mobilization has been widely reported to decrease the aquifer’s permeability during water flooding. However, previous studies of clay alteration (i.e., dissolution and secondary mineral formation) did not attempt to simulate GCS conditions. To fill this important information gap, it is important to study CO$_2$–brine–clay interactions during and after CO$_2$ injection. Thus, the first general research scope was to study CO$_2$-brine–clay interactions under various conditions relevant to GCS sites. Biotite, Fe-bearing mica, was chosen in this study for several reasons: first, mica has perfect cleavage along the (001) plane, making it easy to obtain a flat mica basal surface for measuring surface morphological evolutions after CO$_2$-brine–mica interactions. Second, biotite has much faster dissolution rate at acidic conditions than other mica minerals of muscovite and phlogopite.$^{19}$ Third, biotite contains both Fe(II) and
Fe(III), they can have redox reactions with the impurity gases (e.g., SO₂, H₂S) injected together with CO₂.

Also, regarding CO₂–brine–rock interactions under GCS conditions, mineral dissolution and precipitation happens at the same time. However, most current research has focused on mineral dissolution kinetics. The precipitation kinetics, especially the heterogeneous precipitation kinetics, are rarely studied because of the difficulty in quantifying the amount of precipitates both in solution (homogeneous precipitation) and on the substrate (heterogeneous precipitation). Mineral precipitation could affect the brine compositions and alter porosity and permeability, while secondary mineral coating on pre-existing rocks could alter the wettability and reactivity of the pre-existing rock. Thus, a better understanding of precipitation kinetics at brine (water)-rock interfaces is essential for accurate reactive transport modeling in porous media.

At GCS field sites, increases in the concentrations of Fe and the originally adsorbed pollutants in the aquifer were observed near the injection sites. As the acidic brine flowed and mixed with the originally neutral brine, Fe precipitation and absorption of the aqueous pollutants occurred. If CO₂ leaks from the reservoir, the degassing of CO₂ will bring up the pH of the brine, resulting in heterogeneous Fe precipitation on rocks, which can absorb and immobilize the pollutants in the brine, reducing the pollution of groundwater. To better understand the fate and
transport of aqueous pollutants in aquifers, another general research scope is to study the homogeneous and heterogeneous nucleation and growth kinetics of Fe(III) (hydr)oxides in solution and at brine (water)-rock interfaces. Quartz, mica, and sapphire were chosen as substrate minerals for heterogeneous precipitation because of their abundance at GCS sites and their distinct surface structures and properties, which can affect heterogeneous precipitation.

1.2.2 Specific Research Objectives

The first research scope, CO₂–brine–mica interactions under relevant GCS conditions, will be explored in two steps, described below as Objectives 1 and 2. The second research scope, *in situ* nucleation and growth kinetics of Fe(III) (hydr)oxides in solution and at brine (water)-rock interfaces, corresponds to Objectives 3 and 4.

**Objective 1**: Elucidate the coupled dissolution and secondary mineral precipitation under hydrothermal conditions at the CO₂–brine–biotite interfaces.

Hypothesis: At GCS sites, the brine contains high NaCl and high dissolved CO₂ concentrations; also, the temperature and pressure are high. Biotite dissolution and secondary mineral precipitation under these conditions would be different from previous studies under low temperature, low CO₂ pressure, and low salt conditions, and these reactions can affect the permeability in aquifers.
**Objective 2:** Determine the effects of temperature, aqueous CO$_2$ concentration, and brine composition on mica dissolution and morphological changes.

Hypothesis: At different GCS sites, the reported environmental conditions varied greatly, such as temperature, aqueous CO$_2$ concentration, and brine composition. These conditions would affect biotite dissolution and morphological changes.

**Objective 3:** Quantify both the homogeneous and heterogeneous precipitation kinetics of Fe (hydr)oxides on quartz in the presence of environmentally ubiquitous anions (NO$_3^-$, Cl$^-$, and SO$_4^{2-}$).

Hypothesis: The precipitation kinetics of Fe(III) (hydr)oxides can be affected by the presence of different anions. At GCS sites, there are high Cl$^-$ and SO$_4^{2-}$ (Table 1.1) concentrations, which will affect the precipitation kinetics of Fe(III) (hydr)oxides, thus affecting the pollutant transport.

**Objective 4:** Quantitatively analyze the effect of quartz, mica, and sapphire on heterogeneous nucleation and growth kinetics of Fe(III) (hydr)oxides and elucidate the controlling mechanism.

Hypothesis: The different minerals existing as the substrate will affect the heterogeneous nucleation and growth kinetics due to different surface structures, charges, and hydrophilicities.
1.3 Dissertation Overview

**Overview:** In pursuit of the four objectives listed above, four tasks were completed, with each task corresponding to one of the specific objectives. Tasks 1 and 2 determined CO$_2$–brine–mica interactions under varied acidic hydrothermal conditions relevant to different GCS sites. The new findings of these tasks can be used to guide safer and more efficient subsurface operations, including not only GCS, but also managed aquifer recharge (MAR) and other related field site operations. Tasks 3 and 4 quantified the homogeneous and heterogeneous nucleation and growth kinetics at brine (water)–rock interfaces. Because of the technical difficulty in conducting grazing-incidence small angle X-ray scattering (GISAXS) experiments under GCS conditions, the current study was conducted at ambient conditions. However, it can pave the way for future studies under relevant GCS conditions. It can also be applicable for predicting the fate and transport of aqueous pollutants in the groundwater caused by CO$_2$ leakage, as well as at acid mine drainage (AMD) sites.

**Task 1** is addressed in Chapter 2. To mimic GCS conditions, batch experiments were conducted with biotite at 102 atm CO$_2$ pressure and 95°C, and 1 M NaCl solution was used to mimic the brine in deep saline aquifers. Secondary mineral formation and solution chemistry/solid morphology evolution with reaction time were analyzed, and the related mechanisms were discussed.
Task 2 is addressed in Chapters 3 and 4. Batch experiments were conducted with biotite under a wide range of conditions typical at GCS sites (35–95°C, 75–120 atm CO₂ pressure, in water and in NaCl, MgCl₂, and CaCl₂ solutions). Comparison experiments were also conducted under 102 atm N₂ pressure, with and without the pH of the solution adjusted with HCl. The effects of brine composition, temperature, and CO₂ pressure on biotite ion release, the formation of swelling-related morphologies (bump, bulge, and crack), and illite precipitation were investigated, and the mechanisms were discussed. The activation energy of biotite dissolution over the temperature range was calculated based on framework ion release.

Task 3 is addressed in Chapter 5. Simultaneous homogeneous and heterogeneous Fe(III) (hydr)oxide nanoparticle precipitation experiments were conducted with 10⁻⁴ M Fe(III) solution (with 10 mM ionic strength at pH = 3.7 ± 0.2) in the presence of ubiquitous anions (NO₃⁻, Cl⁻, and SO₄²⁻) and quartz. SAXS/GISAXS were employed to quantify in situ the size and volume evolutions of the precipitates. The size and volume evolutions of the precipitates in the presence of different anions and substrates were compared, and the related mechanisms were elucidated.

Task 4 is addressed in Chapter 6. Fe(III) (hydr)oxide nanoparticle precipitation experiments on quartz, mica, and sapphire were conducted with 10⁻⁴ M Fe(III) solution (in 10 mM NaNO₃ at pH = 3.7 ± 0.2). GISAXS experiments were conducted to quantify in situ the size
and volume evolutions of the precipitates, then the heterogeneous nucleation and growth rates of Fe(III) (hydr)oxides were calculated. To elucidate the mechanisms, supplementary surface characterization techniques (such as water contact angles and zeta potentials) were employed to measure the physico-chemical properties of the substrate surfaces and the precipitates. The controlling mechanisms for heterogeneous nucleation and growth were discussed.

Finally, in Chapter 7, the major conclusions and implications of the current work were summarized, and future directions were recommended.
Chapter 2. Biotite–Brine Interactions: Fibrous Illite, Goethite, and Kaolinite Formation and Biotite Surface Cracking

Results of this chapter have been published in Environmental Science & Technology, 2011, 45(14), 6175 – 6180.

Abstract

To ensure safe and efficient geologic CO₂ sequestration (GCS), it is crucial to have a better understanding of CO₂–brine–rock interactions under GCS conditions. In this study, using biotite \((\text{K(Mg,Fe)}_3\text{AlSi}_3\text{O}_{10}(\text{OH,F})_2)\) as a model clay mineral, brine-biotite interactions were studied under conditions relevant to GCS sites (95°C, 102 atm CO₂, and 1 M NaCl solution). After reaction for 3–17 h, fast growth of fibrous illite on flat basal planes of biotite was observed. After 22–70 h reaction, the biotite basal surface cracked, resulting in illite detaching from the surface. Later on (96–120 h), the cracked surface layer was released into solution, thus the inner layer was exposed as a renewed flat basal surface. The cracking and detachment of the biotite surface layer increased the surface area in contact with solution and accelerated biotite dissolution. On biotite edge surfaces, Al-substituted goethite and kaolinite precipitated. In control experiments with water under the same temperature and pressure, neither macroscopic
fibrous illite nor cracks were observed. This study provides unique information on biotite-brine interaction under acidic hydrothermal conditions.

2.1 Introduction

Long-term geologic CO₂ sequestration (GCS) in deep saline aquifers is one of the most promising options for decreasing CO₂ concentration in the atmosphere.¹ During and after CO₂ injection, CO₂–brine–rock interactions might promote significant geochemical reactions, which could alter the brine compositions and cause porosity, permeability, reactivity, and wettability changes of the caprock and formation rock.¹¹ These changes will influence the seal integrity and CO₂ injectivity, which are essential for safe and efficient GCS.

To prevent CO₂ leakage, it is important to maintain the seal integrity of the caprock. Clay minerals are a major component of caprock at GCS sites.¹⁸ However, little research has been done on CO₂–brine–clay interactions under GCS conditions.²²-²⁴ In this study, biotite was used as a model for clay minerals found at GCS sites.²⁵ Previous studies on biotite alteration (i.e., biotite dissolution and secondary mineral formations) are summarized in Table 2-S1 in Supporting Information. Different dissolution stoichiometries and a variety of alteration products have been observed under diverse environmental conditions.²⁶-³² Although these previous studies provide good background information, none of them have attempted to simulate GCS conditions. For CO₂ storage in deep saline aquifers, the relevant conditions are high temperature (31 °C ≤ T ≤ 39°C) and acidity (pH 1-5) conditions.
110 °C, high pressure (72.8 < P ≤ 592 atm), high salt concentrations (0.01 ≤ NaCl ≤ 2 M), and relatively acidic pH which ranges from 3–5 near injection sites.

Thus, the objective of this research was to understand the effect of brine–biotite interactions under relevant GCS conditions on the aqueous chemistry, interfacial topography changes, and secondary mineral formation. To mimic GCS conditions, experiments were conducted under 95˚C and 102 atm CO₂. One molar NaCl solution was used to mimic brine in deep saline aquifers because Na⁺ and Cl⁻ have the highest concentrations among cations and anions in deep saline aquifer.

### 2.2. Experimental Section

#### 2.2.1 Minerals

Biotite single crystals were obtained from Ontario, Canada (Ward’s Natural Scientific). X-ray diffraction data confirmed the sample as pure biotite. Based on electron microprobe (EMP) and X-ray fluorescence (XRF) measurements, the elemental composition of the biotite sample was $K_{0.91}Na_{0.08}(Mg_{0.52}Mn_{0.02}Fe_{0.37}Ti_{0.04})_3(Al_{1.00}Si_{3.00})O_{10}(F_{0.43}(OH)_{0.57})_2$. A Fe(II)/Fe(III) ratio of 5:1 was determined using the hydroxylamine and ferrozine method.

#### 2.2.2 High Pressure and Temperature Reaction
A bench-top reactor (Parr Company, IL) was connected to a syringe pump (Teledyne ISCO, Lincoln, NE) to conduct high pressure and temperature batch experiments (102 atm, 95°C). Thin flakes of biotite (101 ± 21 µm thick) were prepared by cleaving along the {001} planes (basal planes) and cutting them into 2.5 cm × 0.8 cm rectangles. The mass of a single flake was 0.015 ± 0.003 g. Batch experiments were conducted with one biotite flake and 4 ml of 1 M NaCl solution. After reaction (elapsed times were 3, 5, 8, 17, 22, 44, 70, 96, and 144 h), the dissolved ion concentrations in solution were measured by inductively coupled plasma-mass spectrometry (ICP-MS, 7500ce, Agilent Technologies, CA). The reacted biotite basal surfaces were studied with optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). The in situ pHs were measured with pH probes (Corr Instrument, TX) operating at 102 atm and 95°C with the same water/rock ratio (20 pieces of biotite flakes in 80 ml solution) of these batch experiments.22 The experimental setups of batch reactions and in situ pH measurements are shown in Figure 2-S1 and 2-S2 (Supporting Information).

To facilitate the observation of secondary minerals that formed on biotite edge surfaces, additional batch experiments were conducted with thick biotite crystals (thickness: 5 mm) for 7 days. To observe the effects of NaCl, control experiments were conducted in deionized water with biotite. Before reaction, clean basal planes (Figures 2.1A and 2.2A) and edge surfaces of biotite (Figure 2.2B) were observed.
2.2.3 Identification of Secondary Mineral Phases

SEM-EDX (energy-dispersive X-ray spectroscopy) was used to observe the shape and elemental compositions of the precipitates. For EDX measurements of the precipitates on biotite surfaces, a low accelerating voltage of 3 kV was selected to reach a lower penetration depth. Thus, we could collect more quantitative elemental compositions of the precipitates on the sample surface rather than from the bulk. For fibrous illite on basal planes, additional steps have been taken because even at 3 kV, the penetration depth of the X-ray was still higher than the thickness of the fibrous illite (around 20–200 nm, measured by AFM). Thus, to obtain better elemental compositions of the illite without the influence of the biotite substrate, the fibrous illite was detached from the reacted biotite substrate by sonication, and a droplet of the supernatant was prepared on a formvar/carbon coated-Cu grid for EDX measurement at 10 kV.

To measure the atomic d-spacings for mineral phase identification of these precipitates on the reacted surface, reacted biotite samples were measured with high resolution-transmission electron microscopy (HR-TEM, JEOL JEM-2100F field emission). Samples were sonicated for 30 min to detach the precipitates from the surface, and a drop of this suspension was placed on a formvar/carbon coated-Cu grid. To identify the mineral phases in the reacted solution, the sample suspension reacted with a biotite flake for 144 h was also analyzed by HR-TEM.
2.3. Results and Discussion

After pressurized CO$_2$ (102 atm) was introduced for 1 hr, the *in situ* pH of the CO$_2$–1 M NaCl–biotite flake system at 95˚C was 3.1 ± 0.1. During the following 144 h, the pH increased gradually to 3.6 ± 0.1 due to biotite dissolution. After reaction for each elapsed time, the ion concentrations measured by ICP-MS were used as input values to Geochemist’s Workbench (GWB, Release 8.0, RockWare, Inc.) for calculations of the pH values and the saturation indices (SI) of potential secondary minerals. The calculated pH values were 3.26 right after CO$_2$ injection, and 3.77 after 144 h reaction, which are generally consistent with the *in situ* pH measurements.

After reaction with biotite flakes, optical microscopy was used to observe the basal surfaces of all the biotite flakes (cm scale, Figure 2-S3), while AFM provided the 3D topographical information (μm and nm scale). Throughout the reaction (3–144 h), three types of surfaces were observed. After reaction for 3–17 h, a flat biotite basal surface with numerous fibrous precipitates was observed (type 1, Figure 2.1B). After 22–70 h reaction, the biotite surface layer cracked into micro segments, and only a few fibrous precipitates were observed (type 2, Figures 2.1C, 2.1D). After 96 h reaction, some micro-segments of the cracked biotite surface layer detached, and the remaining segments of the cracked surface layer were resting on a flat inner layer (type 3, Figure 2.1E).
Figure 2.1. Observations of biotite basal planes with contact mode AFM before and after reaction of single biotite flakes in 1 M NaCl at 95°C and 102 atm CO$_2$ for different times. The height profiles below the AFM images are cut along the white dashed lines in the AFM images. The cartoon as an inset in Figure C shows the swelling caused by Na$^+$–K$^+$ ion exchange. The dots represent interlayer K$^+$ in biotite, and the triangles represent the hydrated Na$^+$ that entered the biotite interlayer through ion-exchange.

Later on (120 h), a flat biotite basal surface bearing abundant fibrous precipitates was observed again as type 1, which indicates that the cracked biotite surface layer totally detached and released into solution, completely exposing the inner flat layer as a renewed basal surface. Thus, a new cycle of morphological evolutions began. After reaction for 144 h, a cracked biotite surface layer was observed again as type 2. The images collected after reaction for 120 and 144 h were similar to Figure 2.1B and Figure 2.1C, and they are shown in Figure 2-S4 in the
Supporting Information). A more detailed description of these three types of surface morphologies follows in Sections 3.1 and 3.2.

<table>
<thead>
<tr>
<th>Basal planes</th>
<th>Edge surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Control</strong></td>
<td><strong>Control</strong></td>
</tr>
<tr>
<td>5 μm</td>
<td>10 μm</td>
</tr>
<tr>
<td>2 μm</td>
<td>1 μm</td>
</tr>
<tr>
<td>3 h</td>
<td>7 days</td>
</tr>
<tr>
<td>6 days</td>
<td>7 days</td>
</tr>
</tbody>
</table>

**Figure 2.2.** Observations of biotite basal planes (Figures A, C, E) and edge surfaces (Figures B, D, F) by SEM-EDX before and after reaction of thin biotite flakes (Figure A, C, E) and thick biotite crystals (Figure B, D, F) in 1 M NaCl solution at 95°C and 102 atm CO₂. EDX patterns (I, II, III, IV) were collected at the spots indicated by the arrows. An SEM image of the fibrous illite on the formvar/carbon coated-Cu grid after sonication is shown in the inset of Figure E. The Cu and high C peaks shown in the EDX pattern (II) come from the grid.

2.3.1 Fibrous Precipitate Formation on Flat Biotite Basal Planes

After reaction for 3–17 h, numerous fibrous precipitates were observed on the flat biotite basal plane (type 1, Figure 2.1B). Some of the fibrous precipitates intersected at a 120° angle. Based on AFM image analysis of 50 fibrous precipitates, the length, width, and thickness of these fibrous precipitates varied over a broad range, and were approximately on the order of 30, 1, and 0.05 μm, respectively. D-spacings of these fibrous precipitates measured by HR-TEM
(10.03, 3.86, 3.14, 2.39, 2.09, and 1.43 Å) showed a good match with illite (Figure 2.3A).\textsuperscript{34} Chlorite, vermiculite, smectite, kaolinite, and corrensite—the most commonly reported products of biotite alteration under acidic conditions\textsuperscript{26-28,32}—do not have the 10.03 Å d-spacing.\textsuperscript{34} Hence, these minerals were ruled out as possible candidates for the precipitates observed here. In addition, the thin and long fibrous precipitates observed in this study was similar to previous reports on fibrous illite’s morphology.\textsuperscript{35} The 120° angle intersection of the fibrous precipitates observed in this study was also consistent with a previous observation of fibrous illite grown on mica core in Rhourde el Baguel Sandstone.\textsuperscript{36} Thus, the fibrous shape, the 120° angle, and the d-spacings of these precipitates confirmed that they are illite.

![Figure 2.3. Precipitate phase identification by HR-TEM. Fibrous illite (A), Al-substituted goethite (B), and kaolinite (C) are identified.](image-url)

Interestingly, however, GWB calculations showed that the solution was undersaturated with illite throughout the experimental period. Two processes could have contributed to the unexpected illite precipitation. First, in our unstirred batch system, compared with the bulk solution, the local dissolved ion concentrations near the biotite surface could be higher and be
supersaturated with respect to illite. Second, fibrous illite has the same monoclinic crystal structure as biotite. There are less than 3.1% lattice mismatches between biotite and illite. There will be only a small lattice mismatch for the heteroepitaxial nucleation of fibrous illite on biotite. Therefore, compared with homogeneous nucleation calculated by GWB, lower dissolved ion concentrations could be required for heterogeneous nucleation of fibrous illite on biotite to occur.

For control experiments conducted in deionized water, optical microscopy was employed to observe all reacted biotite basal surfaces. No macroscopic fibrous illite was observed throughout the reaction (3–144 h). The lack of macroscopic fibrous illite formation in water can be related to the slower biotite dissolution occurring in water. In 1 M NaCl, higher dissolved ion concentrations, especially K\(^+\), was observed (Figure 2.5) than in water. The dissolved K\(^+\) concentrations in 1 M NaCl solution were around 30–40 times higher than those in water, because the H\(^+\)–K\(^+\) ion exchange in water is much slower than the Na\(^+\)–K\(^+\) ion exchange in 1 M NaCl solution. Measured EDX data (Figure 2.2II) confirmed that the fibrous illite contains K, Mg, Fe, Al and Si (Figure 2.2E). Thus, the fast release of these ions in 1 M NaCl solution could cause the local solution near the biotite surface to be supersaturated with respect to illite, promoting illite precipitation.
Most previous laboratory experiments of biotite alteration were conducted in solutions with low salt concentrations (Table 2-S1).\textsuperscript{27,28,32} Some investigations were done under high salt concentrations and high pH conditions, to mimic nuclear waste disposal conditions (Table 2-S1).\textsuperscript{30,31} Those experimental conditions are different from GCS conditions and no fibrous illite formation was reported. In our experiments of biotite alteration under relevant GCS conditions (95°C and 102 atm CO\textsubscript{2}, in 1 M NaCl solution, and pH \textasciitilde 3.1–3.6), significant amounts of macroscopic fibrous illite precipitates were observed after reaction for only 3 h. To the best of our knowledge, this is the first time that fast fibrous illite precipitation on biotite basal planes was directly observed in laboratory biotite alteration experiments. This finding indicates that a better understanding of brine–clay interactions at GCS sites requires conducting experiments under relevant conditions. Furthermore, more research on the mechanisms of fibrous illite formation and the influence of different environmental conditions is needed.

2.3.2 Cracking and Detachment of Biotite Basal Surface Layers and Detachment of Fibrous Illite

During 22–70 h reaction, cracking of the biotite surface layer occurred (type 2, Figures 2.1C, 2.1D). Based on AFM analysis of 20 cracks, the crack depths were around 13.4 ± 5.0 nm after reaction for 22 h (Figure 2.1C), which increased to 31.2 ± 5.7 nm after reaction for 44 h (Figure 2.1D), and increased further to 57.5 ± 7.6 nm after reaction for 70 h. Later, the cracked
surface layers gradually detached from the biotite crystals. Cracking and the resulting detachment of the biotite basal surface have been documented, and are thought to be related to K$^+$-release from the interlayer, and a release of internal stresses.$^{39}$ Previous work by our group showed that ion-exchange of aqueous Na$^+$ with interlayer K$^+$ in phlogopite—Mg-end member mica which has the same crystal structure as biotite—caused a swelling of phlogopite, and the layer thicknesses of phlogopite increased from 1 nm to 1.20–1.60 nm (A cartoon is shown as the inset in Figure 2.1C.).$^{23}$ In our system, Na$^+$–K$^+$ ion-exchange also occurred as described in Section 3.1. A schematic diagram of the cracking and detachment of the biotite surface layer caused by Na$^+$–K$^+$ ion-exchange is shown in Figure 2.4. Defects, where ion exchange and swelling were reported to occur faster,$^{40}$ could exist on the biotite basal plane (Figure 2.4A). Thus, the enhanced swelling around these defects resulted in a bent surface. Internal stress could build up in the bent surface, resulting in the cracking (Figures 2.1C, D and Figures 2.4B, C) and detachment of the surface layer (Figures 2.1E and 2.4D, E). Also, swelling is reported to be more pronounced for surface layers than inner layers.$^{23}$ Thus, only the biotite surface layer cracked, and the inner layer remained flat in our study (Figure 2.4E).
Another interesting and consistent observation throughout the reaction (3–144 h) was that numerous fibrous illite always grew on the flat biotite basal surface (e.g., after reaction for 3, 5, 8, 17, and 120 h), while a diminished amount of fibrous illite was always associated with a cracked surface (e.g., after reaction for 22, 44, 70, 96, 144 h). One explanation for this phenomenon is that when the surface cracked, stress could build up between the fibrous illite and the cracked biotite substrate, resulting in the detachment of some fibrous illite. To identify the minerals in reacted solution, the solution after 144 h reaction was analyzed by HR-TEM. Numerous small biotite flakes (from nanometers to micrometers), as well as some fibrous illite, were observed in solution (Figure 2-S7). This observation confirmed that fibrous illite and biotite segments had detached from the cracked surface and released into solution.

For the control experiments conducted in deionized water, no cracks were observed by optical microscopy throughout the reaction (3 to 144 h). In water, $H^+-K^+$ ion-exchange could
occur; however, the swelling effect is reported to be much less significant compared with 1 M NaCl cases.\textsuperscript{23} In our previous study, the phlogopite layer depth was in the range of 1.0–1.2 nm after reaction in water, only slightly greater than unreacted phlogopite (1 nm).\textsuperscript{23} Thus, the internal stress could be much weaker, which explains why no cracking occurred in the control experiments throughout the reaction duration. These observations of the control experiments in water support our explanation that the crack formation in NaCl solution is caused by swelling from Na\textsuperscript{+}–K\textsuperscript{+} ion exchange. Also, the direct comparison experiments showed the important role of NaCl solution on biotite surface morphological evolution.

### 2.3.3 Preferential Al-Substituted Goethite and Kaolinite Precipitation on Biotite Edge Surfaces

On the basal plane (Figure 2.2C) of the reacted biotite flakes, more precipitates, enriched in Fe and Al, are found at step sites than at the terrace. Two processes could explain this phenomenon. First, at the step sites, the edge planes of biotite are exposed to solution. According to a previous study, the dissolution rate at the edge planes of biotite is around 250 times higher than at the basal plane.\textsuperscript{41} Thus, local dissolved ion concentrations are likely higher at step sites, enabling precipitation. Second, less free energy is required to form heterogeneous precipitates at step sites.\textsuperscript{42}
To further identify these precipitates, thick biotite crystals with more edge surfaces were reacted under the same conditions for 7 days. Abundant microscale needle-shaped crystal aggregates (Figure 2.2D), containing almost only Fe and Al (Figure 2.2III), were observed on the edge surfaces of all these samples. The needle-shaped morphology, the EDX pattern, and the d-spacing measurements by HR-TEM (Figure 2.3B) confirmed that these precipitates were Al-substituted goethite. Also, on the edge surface, flat precipitates (Figure 2.2F) with an EDX pattern containing almost only Al and Si (Figure 2.2IV) were observed. The morphology, EDX pattern, and d-spacing analysis by HR-TEM (Figure 2.3C) confirmed that the flat precipitates were kaolinite. No fibrous illite was observed on the reacted edge surfaces. Compared with the basal plane, structurally different atomic arrangements and dangling bonds are present on the edge surfaces. In addition, the edge surfaces of the prepared thick biotite samples are quite rough (millimeter scale roughness), with higher physico-chemical discontinuity and irregularity. Therefore, although illite may form at nanoscale, it would not likely grow to μm or mm-scale fibrous illite due to a lack of continuous physical or chemical support. For control experiments conducted in deionized water with thick biotite crystals, needle-shaped Al-substituted goethite and flat kaolinite crystals were also observed on the edge surfaces.

2.3.4 Aqueous Chemistry Evolution and Linkages with Solid Alterations
In addition to understand the surface morphological changes and secondary mineral formation, it is also important to link these changes with aqueous chemistry evolution. As discussed before, three types of morphologies were observed on the basal planes of biotite flakes. Likewise, the leaching rates of the framework ions (Mg, Fe, Al, and Si) from biotite flakes showed three steps (indicated as step I, II, and III by the dashed lines in Figure 2.5). During reaction for 3–17 h (step I), a linear relationship between dissolved ion concentrations with time was observed, indicating a constant dissolution rate. During reaction for 22–70 h (step II), higher leaching rates than in step I were observed for all framework ions. This is consistent with the cracking of the biotite surface after reaction for 22 h (Section 3.2) and the resulting increase in surface area. During reaction for 96–144 h (step III), further increases in the leaching rates for all framework ions were observed compared with step II. This is because the detachment of biotite fragments after reaction for 96 h (Section 3.2) further increased the surface area in contact with solution. Compared with control experiments in water where no cracking was observed, the dissolved interlayer K⁺ concentration was around 30 times higher after reaction in 1 M NaCl for 144 h, and the concentrations of dissolved framework ions were around 10 times higher.
Figure 2.5. Dissolved ion concentrations in 1 M NaCl solution after reaction of single biotite flakes at 95°C and 102 atm CO₂. To check the congruency of biotite dissolution, concentrations are normalized according to the stoichiometry of the different ions in biotite

(K₀.₉₁Na₀.₀₈(Mg₀.₅₂Mn₀.₀₂Fe₀.₃₇Ti₀.₀₄)₃(Al₁₀₀Si₃₀₀)O₁₀(F₀.₄₃(OH)₀.₅₇)₂). For example, for K, the concentrations shown in this figure are the dissolved K concentrations in solutions divided by 0.91.

Regarding the effects of secondary mineral precipitation on aqueous chemistry evolution, fibrous illite having a similar elemental composition (Figure 2.2II) with biotite (Figure 2.2I) was the main precipitate on the basal surface. Al-substituted goethite containing only Al and Fe was the main precipitate on the edge surfaces. This is consistent with the observation that the dissolved Fe and Al concentrations were lower than Mg and Si according to their stoichiometry in biotite (Figure 2.5).
In this study, batch experiments of biotite alteration in 1 M NaCl solution at 95°C and 102 atm CO$_2$ were conducted. Fast macroscopic fibrous illite precipitation on the flat biotite basal plane and its later detachment from the cracked surface were observed while Al-substituted goethite and kaolinite formed at edge surfaces. The fibrous shape makes the specific surface area (area per solid volume) of fibrous illite at least two orders of magnitude higher than bulk crystals.$^{43}$ Thus, the fibrous illite could significantly increase flow-path tortuosity, extend deep into pores, and could cause a large permeability reduction for a given bulk volume. Fibrous illite growth in sandstone reservoirs has been reported to severely decrease the porosity and permeability of the reservoir, resulting in serious problems for hydrocarbon production.$^{36}$

Significant differences were observed for biotite alteration in 1 M NaCl and water, regarding macroscopic fibrous illite formation, basal surface cracking, and dissolution rates. These observations showed the importance of conducting experiments under conditions relevant to GCS conditions with high NaCl concentrations. Although this study focused on GCS conditions, the current findings about coupled biotite dissolution, morphological change, and secondary mineral precipitation could also aid studies of biotite behavior under other conditions, such as nuclear waste disposal, seawater encroachment, and aquifer recharge.
Acknowledgments

This work is supported by the Consortium for Clean Coal Utilization and a Washington University Faculty Start-up Grant. Y.H. and Y.S.J. are partially supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy, in association with the Energy Research Frontier Center (EFRC) of Berkeley Lab, under Contract No. DE-AC02-05CH11231. We would like to acknowledge Washington University’s Center for Materials Innovation (CMI) for use of HR-TEM and Nano Research Facility (NRF) for use of SEM-EDX. We wish to thank Glenn A. Waychunas, Hongbo Shao, Liange Zheng, Yi Yang, and Daniel Garcia for valuable discussion, and Paul Carpenter for EMP measurements.
Supporting Information for Chapter 2

Contents: Experimental details

Three tables (2-S1–2-S3)

Twelve figures (2-S1–2-S12)

Chemicals and Minerals

All chemicals used were at least ACS grade. All solutions were prepared with ultrapure water (18.2 MΩ). The biotite flakes were sonicated in ultrapure water for 30 min to remove small biotite detritus from the surface. Then, the flakes were soaked sequentially in acetone, ethanol, and isopropanol continuously for 5 minutes each to remove any organics on the surface. Finally, the crystals were washed with ultrapure water several times and dried with N₂ gas.

High Temperature and Pressure Reaction

The experimental setup is shown in Figure 2-S1. A bench top reactor, made of Hastelloy C (Parr Company, IL), was connected to a syringe pump (Teledyne ISCO, Lincoln, NE). A temperature controller and thermocouple were used to maintain the reactor at a constant temperature. For conducting batch experiments, CO₂ was pressurized by the syringe pump and introduced into the reactor, and the reactor was held under 1500 psi and 95°C for different time spans. After reaction, the reactor was cooled to room temperature and the CO₂ was released. Then the solutions were filtrated through 0.22 μm filters and were acidified for ICP-MS measurement. The biotite flakes were washed with DI water, and were then dried gently with N₂ gas.
Reports of other studies have shown contamination from the dissolution of reactor material. In this study, to prevent the interference of materials dissolved from the reactor, biotite and solutions (1 M NaCl or water) were placed in Teflon test tubes, and then all test tubes were put in a Teflon liner inside the reactor. An FEP sheet (covering the top of the liner) was applied inside the reactor to avoid contamination caused by dissolution of the reactor material in the presence of CO₂. For each batch, a blank was tested by adding water in a test tube without biotite. Based on ICP-MS results of the blank for all batch experiments, no contamination was detected.

For the biotite experiments conducted in 1 M NaCl and in water, exactly the same experimental procedure was used, and significant differences regarding surface morphological evolution of the reacted biotite and the dissolved ion concentrations were observed after reaction. Therefore, these differences were caused by reaction inside the reactor instead of being artifacts coming from experimental procedure.

For in situ pH measurements, 20 pieces of biotite flakes were put into 80 ml of 1 M NaCl solution (the same rock/water ratio as 1 piece of biotite flake and 4 ml solution, 0.015 g/4 ml), and were reacted under the same conditions (102 atm, 95°C) for 6 days (Figure 2-S2). The calibration of the pH probe was done with different HCl concentrations in 1 M NaCl solutions.

Calculations of the pH Values and Saturation Indices of Potential Minerals with Geochemist’s Workbench (GWB)

To calculate the initial pH right after CO₂ injection, 1 M NaCl was added as the basis species in Geochemist’s Workbench (GWB, Release 8.0, RockWare, Inc.). The temperature was set as 95°C. The fugacity coefficient of CO₂ was calculated as a function of pressure, temperature,
and ionic strength according to the literature.\textsuperscript{45} The CO\textsubscript{2} fugacity, calculated as the product of the CO\textsubscript{2} pressure and the fugacity coefficient, was also included as a basis species for GWB calculations. According to the GWB manual,\textsuperscript{46} the ion size parameter of CO\textsubscript{2(aq)} in the database was assigned to be -0.5, so the salting-out effect of CO\textsubscript{2} as a function of ionic strength was calculated. The activity of each dissolved species was calculated as the product of the concentration and the activity coefficient. The B-dot equation was used for activity coefficient calculations. The equation is considered reasonably accurate in predicting the activities of Na\textsuperscript{+} and Cl\textsuperscript{-} ions to concentrations as large as several molal, and of other species to ionic strengths up to about 0.3 to 1 molal.\textsuperscript{47} Therefore, it is sufficient to use this equation for activity calculations in our system. The setting of these basis species simulated the 1 M NaCl–CO\textsubscript{2} solution right after CO\textsubscript{2} injection. Based on charge balance, this initial pH was calculated to be 3.26.

After reaction for each elapsed time, the dissolved ion concentrations increased during biotite dissolution, thus, the pH of the solution and the saturation indices (SI) for potential minerals changed. The dissolved ion concentrations (including K, Mg, Fe, Al, and Si) in the bulk solution at each elapsed time were measured by ICP-MS. These dissolved species concentrations were added into the basis. The pH of the solution after reaction for each elapsed time was calculated based on charge balance, and the saturation indices for potential minerals were also calculated.

Fibrous illite precipitation was observed after reaction for 3 hrs, when the bulk solution was undersaturated. This precipitation could have occurred because the local dissolved ion concentrations near the biotite surface were higher than those in the bulk solution in our unstirred system. GWB calculations showed that after 3 h reaction, assuming the local dissolved ion
concentrations near the biotite surface are 25 times higher than those measured by ICP-MS in the bulk solution, the local solution is supersaturated with respect to illite.
Main Chemical Reactions

The main chemical reactions are as follows (stoichiometries of the chemical species are not balanced):

1) Biotite dissolution

\[
\text{Na}^+ - \text{K}^+ \text{ ion exchange resulting in K-leached biotite:}
\]

\[
\text{K(Mg, Fe)_3AlSi}_3\text{O}_{10}(\text{OH, F})_2 \text{ + Na}^+ \rightarrow \text{Na(Mg,Fe)}_3\text{AlSi}_3\text{O}_{10}(\text{OH, F})_2 \text{ + K}^+
\]

\[
\text{Dissolution of framework ions of biotite:}
\]

\[
\text{Na(Mg, Fe)_3AlSi}_3\text{O}_{10}(\text{OH, F})_2 \text{ + H}^+ \rightarrow \text{Na}^+ \text{ + Mg}^{2+} \text{ + Fe}^{2+} \text{ + Fe}^{3+} \text{ + Al}^{3+} \text{ + Si}^{4+} \text{ + F}^- \text{ + H}_2\text{O}
\]

2) Illite precipitation

\[
\text{K}^+ \text{ + Mg}^{2+} \text{ + Fe}^{2+} \text{ + Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{K(Al, Mg, Fe)}_2(\text{Si, Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})] + \text{H}^+
\]

3) Al-substituted goethite and kaolinite precipitation

\[
\text{Fe}^{3+}\text{+Al}^{3+} + \text{H}_2\text{O} \rightarrow (\text{Al, Fe})\text{OOH + H}^+
\]

\[
\text{Al}^{3+} \text{ + Si}^{4+} + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{H}^+
\]

Morphological Changes on Biotite Basal Planes

After reaction for different times, the morphological evolutions of the reacted biotite surfaces were observed with optical microscopy and contact mode atomic force microscopy (AFM). Representative images are shown in Figure 2-S3 and 2-S4, respectively. In other studies of sheet silicate, dendritic shaped bulges formed by swelling have been observed, having similar morphology to the fibrous precipitates observed in this study.\textsuperscript{40,48} To better observe the detailed
features of the fibrous structure in our study, tapping mode AFM was also used, and more than 200 tapping mode AFM images were scanned for samples after reaction at 1500 psi CO₂, and 95°C in 1 M NaCl for different hourly durations. Both fibrous-shaped precipitates and dendritic-shaped bulges were observed, although the bulge formation was very rare. Based on tapping mode AFM images (Figure 2-S5 and vS6), the fibrous structures on the biotite surface in our study are secondary mineral precipitates instead of bulges caused by swelling. As shown in Figure 2-S5, two sets of images (Sets 1 and 2) collected at two spots after reaction in 1 M NaCl solution under 1500psi CO₂ at 95°C for 3 hrs were chosen as examples showing the detailed features of the fibrous structure. For Sets 1 and 2, the middle part and the end of the fibrous structure were zoomed in (Sets 1B and 2B, respectively). Clearly shown in both sets of images, the fibrous structure is formed by the aggregation of nano-scale precipitates following the crystallographic direction of the substrate. Several nano-precipitates were cut in both Sets 1B and 2B along the dashed lines, and they are pointed out by the drawings in the phase images, as well as the arrows in the height cross sections. Based on these images, the fibrous shaped structures are secondary mineral precipitates instead of bulges.

The aggregation of small particles forming the fibrous structure on the biotite basal plane was also observed after reaction in 1 M NaCl solution, under 1500 psi CO₂, at lower temperatures (55 and 65 °C) (unpublished work). Three representative images are shown in Figure 2-S6. Although they were not obtained under exactly the same experimental conditions as this study, the experimental conditions were quite similar. Under these conditions, a little slower reaction is expected. The aggregation of small precipitates forming the fibrous shaped structure is also clearly shown in these images.
In this study, based on over 200 tapping mode AFM images, only two images showing dendritic shaped bulges were observed, and predominantly numerous fibrous precipitates were observed. Comparison between the dendritic–shaped bulges and the fibrous–shaped precipitates observed in our system is shown in Figure 2-S7. The height, amplitude, and phase mode images show clearly the different shapes of the fibrous precipitates and the dendritic bulges. In many previous studies, the differences in the phase shifts in phase mode images have been used to differentiate components in composite materials, especially between products and original materials.\textsuperscript{49-54} Different crystal structures and mechanical properties on the surface can result in differences in the phase shifts. As shown in Figure 2-S7, the difference in the phase shifts between the fibrous structure and the flat biotite ranges from 38 to 85º, while the difference in the phase shifts between the bulge and the flat biotite is within 20º. Because the bulges are caused by swelling, they are the same biotite phase with more strain and stress. Thus, there is a relatively small difference in the phase shifts between the bulge and the flat biotite. On the other hand, the fibrous precipitates are secondary mineral phases different from biotite. Therefore, there can be a much larger difference in the phase shifts between the fibrous precipitates and the flat biotite. Furthermore, the phase shift profile curves are relatively smooth for the flat biotite surface and the bulges, while large fluctuations are exhibited for the fibrous precipitates. It is likely that the aggregation of nano-scale precipitates on the fibrous structure resulted in the large fluctuation in the phase shift profile.

To sum up, the fibrous structures are formed by aggregation of nanoparticles. Also, significant differences in shape and phase shift exist between the fibrous precipitates and the dendritic bulges. After considering all the evidence, we confirmed that in our system the fibrous structures are fibrous precipitates instead of dendritic bulges caused by swelling.
Comparison between the dendritic shaped bulges and the fibrous-shaped precipitates observed in our system is shown in Figure 2-S7. The amplitude mode image shows clearly the different shapes of the fibrous precipitates and the dendritic bulges. The AFM phase images have been used to differentiate components in composite materials, especially between products and original materials.\textsuperscript{49-54} In Figure 2-S7, the phase image profiles show clearly that there is a larger phase shift from biotite for the fibrous precipitates than the bulges. Because the bulges are caused by swelling, they are similar in mineral phase to biotite. On the other hand, the fibrous precipitates are secondary mineral phases. Therefore, there can be much larger phase shifts from biotite. Furthermore, the phase profile curves are relatively smooth for the flat biotite surface and the bulges, while large fluctuations are exhibited by the fibrous precipitates. This fluctuation is because the fibrous precipitates are formed by the aggregation of small precipitates, as discussed above. These images show clearly the differences in shape, phase shifts from biotite, and the fluctuations in phase profiles between the fibrous precipitates and the dendritic bulges. After considering all the evidence, we confirmed that in our system the fibrous structures are fibrous precipitates instead of dendritic bulges.

The morphology of the “cracks” observed in this study is similar to the “dissolution channels” observed in other studies to some extent. Two types of formation mechanisms for the “dissolution channels” are described in the literatures. In Brandt’s study,\textsuperscript{55} they found that “within the basal surfaces of the chlorite sample subjected to the dissolution experiment, we find channel like features, which may originate from the cracks of the initial sample.” In Brandt’s research, the definition of dissolution channel is the channel structure formed on the basal surface, caused by the preferential dissolution at original cracks on the surface. In another work by our group, the channel-like morphology on the basal plane of phlogopite was also observed.\textsuperscript{22}
In our previous study on phlogopite, the dissolution channel was caused purely by the interconnection of dissolution pits: it formed without initial cracks. Figure 2-S8 (Top) showed the dissolution channels formed on phlogopite after reaction for 159 hrs. In this case, the interconnection of the individual dissolution pits is clearly observed. For comparison, the images of the “cracks” formed in the current study are also shown in Figure 2-S8 (Bottom). The “cracks” on the biotite surface are much deeper and sharper than the “dissolution channels” formed by interconnection of dissolution pits on phlogopite surface. Also, individual dissolution pits along the cracks were not observed. Therefore, to create the morphology observed in the current study, there should be mechanical forces, such as stress in the bent surface, to cause the surface to crack, and the morphology is not likely to form purely by dissolution. Although, when cracking happens, there could be enhanced dissolution at the cracks, as shown in Brandt’s study. Because the cracking of the surface is the most important step which contributes to the morphology formed in the current study, “crack” instead of “dissolution channel” was used to describe the morphology change of the biotite surface.

**Fibrous Precipitate Phase Identification**

The fibrous precipitates were identified as fibrous illite based on their fibrous shape, their growth at 120° intersection, and the TEM d-spacing matching with illite. Although none of this evidence alone could strongly confirm illite formation, it would be hard to find in nature another mineral which has been reported to satisfy all three of these characteristics together. Kaolinite, chloride, smectite, corrensite, and vermiculite are the most commonly reported products of biotite alteration under acidic conditions, as listed in Table 2-S1. Many studies have used HRTEM to identify the products during biotite alteration. Illite, corrensite, smectite, vermiculite, and kaolinite have been identified as biotite alteration products based on HRTEM observations.
The measured d-spacing of 1.003 nm of the fibrous precipitates ruled out the possibility of kaolinite, chloride, smectite, or vermiculite, which do not have a d-spacing within a ±10% error range of 1.003 nm (i.e., 0.9 nm – 1.1 nm). Hydrobiotite has also been reported as an intermediate alteration product of biotite. The term hydrobiotite is used in the literature for poorly-defined biotite material which has been altered to some degree, containing regularly interstratified layers of biotite and vermiculite. Based on these definitions of hydrobiotite, hydrobiotite is formed as an intermediate alteration product followed a layered structure of biotite, and it is not formed by precipitation from solution. Also, fibrous shaped hydrobiotite grown on biotite basal plane has not been reported before. In our AFM observations, the fibrous structures are more likely nanoparticles heteroepitaxially formed on the biotite’s basal surface by dissolution-precipitation. These heteroepitaxial growths can be affected by the crystal structure of the biotite substrate, but they do not have an exact crystal structure and morphology.

Therefore, after ruling out other possible mineral phases, and considering the good d-spacing matching of the fibrous precipitates with illite, as well as taking into account the consistency between the fibrous shape and the 120 degree angle of the fibrous precipitates observed here and that reported in the literature for fibrous illite, we concluded that the fibrous precipitates in our study are fibrous illite.
Figure 2-S1. Experimental setup for the high temperature and high pressure batch experiments.
Figure 2-S2. Experimental setup for the high temperature and high pressure in-situ pH measurements.
**Figure 2-S3** Optical microscopy images of biotite basal planes after reaction in 1 M NaCl solutions at 95°C and 102 atm CO₂.
47
Figure 2-S4. More contact mode AFM images of biotite basal planes after reaction of single biotite flakes in 1 M NaCl under 102 atm CO$_2$ and 95°C for different times. From left to right, the images are in height, deflection error, and friction mode, respectively. The height scales for all the height mode images are the same (200 nm).
Figure 2-S5. Fibrous precipitates on biotite basal plane after reaction for 3 hrs under 1500psi CO$_2$, at 95°C in 1 M NaCl solution. Tapping mode AFM was employed. From left to right, height, amplitude, and phase images are shown. The cross sections on the right are cut along the black dashed lines in the height images.
Figure 2-S6. Fibrous precipitates on biotite basal plane after reaction under 1500psi CO$_2$ in 1 M NaCl solution. The reaction times and temperatures are shown in the images. Tapping mode AFM was employed. From left to right, height, amplitude, and phase images are shown.
Figure 2-S7. Fibrous precipitates and possible dendritic bulges on a biotite basal plane after reaction for 3 hrs under 1500 psi CO$_2$, at 95ºC in 1 M NaCl solution. Tapping mode AFM is employed. From left to right, height, amplitude, and phase images are shown. The cross sections on the right correspond to the profile cut along the dashed lines in the phase images with the same color. The orange line is cut along the flat region on the biotite surface, the blue line is cut along the bulge, and the red line is cut along the fibrous precipitates. These trends are consistent with all fibrous precipitation and bulge features.
Figure 2-S8. Basal surfaces of phlogopite and biotite after reaction under 1500 psi CO\textsubscript{2}, at 95ºC in 1 M NaCl solution. Tapping mode AFM was employed. From left to right, height and amplitude mode images are shown. The cross sections on the right correspond to the cut along the dashed lines in the height images.
Figure 2-S9. TEM micrographs of biotite flakes and fibrous illite existing in bulk solution after 144 h reaction.
Figure 2-S10. Observations of biotite flakes with optical microscopy after reaction in deionized water for different times (3–144 h) under 102 atm CO₂ and 95°C. Neither macroscopic fibrous illite nor cracks are observed on the flat basal surface throughout the experiment.
Figure 2-S11. ICP-MS of dissolved ion concentrations after reaction in water for different times under 102 atm CO$_2$ and 95˚C.
**Figure 2-S12.** SEM-EDX images at the edge surfaces of thick biotite crystals after reaction in deionized water for 9 days under 102 atm CO$_2$ and 95°C. Al-substituted goethite (image A) and kaolinite (image B) are observed. The EDX patterns were obtained at areas indicated by the arrows.
Table 2-S1. Previous studies of biotite dissolution and secondary mineral formation in the laboratory and from field site sample analyses.

### Laboratory experiments:

<table>
<thead>
<tr>
<th>Crystals, Grain sizes (µm)</th>
<th>T (°C)</th>
<th>CO₂ (atm)</th>
<th>Solution Ionic Strength (IS)</th>
<th>pH</th>
<th>Dissolution stoichiometry &amp; alteration products</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystals</td>
<td>24</td>
<td>≤10⁻³.⁵</td>
<td>0.1 M HNO₃</td>
<td>1.1</td>
<td>K&gt;Al, Fe&gt;Mg&gt;Si, amorphous silica</td>
<td>41</td>
</tr>
<tr>
<td>Crystal</td>
<td>150</td>
<td>≤10⁻³.⁵</td>
<td>DI water</td>
<td>N/A</td>
<td>Fe and Al (hydr)-oxides, vermiculite</td>
<td>27</td>
</tr>
<tr>
<td>Powder, 55–106</td>
<td>100</td>
<td>1</td>
<td>Buffer solution, IS=0.067</td>
<td>4.6</td>
<td>Fe(II)-rich vermiculite/smectite (anoxic), Fe(III)- and Al-(hydr)oxides (oxic condition)</td>
<td>28</td>
</tr>
<tr>
<td>Powder, 75–125</td>
<td>25</td>
<td>0, 0.01</td>
<td>Low IS*</td>
<td>2–10</td>
<td>K&gt;Al, Fe, Mg, Si, vermiculite, kaolinite</td>
<td>32</td>
</tr>
<tr>
<td>Powder, &lt;420</td>
<td>22</td>
<td>≤10⁻³.⁵</td>
<td>Low IS*</td>
<td>3–7</td>
<td>K&gt; Mg, Fe&gt;Al, Si (pH=3), vermiculite</td>
<td>56</td>
</tr>
<tr>
<td>Powder, 10–20</td>
<td>22</td>
<td>≤10⁻³.⁵</td>
<td>Low IS*</td>
<td>1–4</td>
<td>K&gt;Mg, Fe&gt;Al&gt;Si,</td>
<td>19</td>
</tr>
<tr>
<td>53–105</td>
<td>22–25</td>
<td>≤10⁻³.⁵</td>
<td>0.055 M Al(NO₃)₃, and/or 2 M or 6 M NaNO₃</td>
<td>10–14</td>
<td>K&gt;Si, Al, Mg&gt;Fe, vermiculite</td>
<td>30</td>
</tr>
<tr>
<td>Powder, &lt;50</td>
<td>50</td>
<td>≤10⁻³.⁵</td>
<td>0–2 M NaOH</td>
<td>7.1–13.7</td>
<td>K&gt;Si, Al, Mg&gt;Fe, zeolite</td>
<td>31</td>
</tr>
</tbody>
</table>

### Field site sample analyses:

<table>
<thead>
<tr>
<th>burial depth (m)</th>
<th>T (°C)</th>
<th>Alteration Products</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>360–370</td>
<td>Earth surface temperature</td>
<td>Biotite(→ Fe²⁺-rich corrensite ) → Fe²⁺-rich smectite/vermiculite → Kaolinite, Fe (hydr)-oxides</td>
<td>26</td>
</tr>
<tr>
<td>135, 452, 714</td>
<td>&lt; 50</td>
<td>Biotite→ Halloysite → Kaolinite or Biotite→ Kaolinite</td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td>Several hundreds</td>
<td>Biotite→ Kaolinite</td>
<td>57</td>
</tr>
</tbody>
</table>
# In these studies, CO$_2$ partial pressures were not specified. These studies were done under atmospheric conditions, and some of these studies used N$_2$/Ar to purge the solutions, so the CO$_2$ partial pressure should not be higher than the CO$_2$ partial pressure in atmosphere ($10^{-3.5}$ atm).

*In these studies, a small amount of acid or base or buffer solution was used to adjust pH, and the IS was not specified, but should be low based on the descriptions.
Table 2-S2. X-ray penetration depth (μm) at 3 and 5 kV for EDX analyses.

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Fe</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>3kV</td>
<td>0.32</td>
<td>0.21</td>
<td>0.26</td>
<td>0.7</td>
<td>0.1</td>
<td>0.59</td>
</tr>
<tr>
<td>5kV</td>
<td>0.6</td>
<td>0.4</td>
<td>0.5</td>
<td>1.3</td>
<td>0.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Table 2-S3. Matching of measured d-spacings of precipitates by HR-TEM with those of references

<table>
<thead>
<tr>
<th>Measured d-spacings of fibrous precipitates (Å)</th>
<th>d-spacings from ref. of illite (Å)(^{58})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.03</td>
<td>10.02231</td>
</tr>
<tr>
<td>3.86</td>
<td>3.8915</td>
</tr>
<tr>
<td>3.14</td>
<td>3.13012</td>
</tr>
<tr>
<td>2.39</td>
<td>2.38522</td>
</tr>
<tr>
<td>2.09</td>
<td>2.08041</td>
</tr>
<tr>
<td>1.43</td>
<td>1.44392</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measured d-spacings of needle-shaped precipitates (Å)</th>
<th>d-spacings from ref. of Al-goethite(Å)(^{58})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.18</td>
<td>4.16771</td>
</tr>
<tr>
<td>3.34</td>
<td>3.36625</td>
</tr>
<tr>
<td>2.45</td>
<td>2.43818</td>
</tr>
<tr>
<td>2.09</td>
<td>2.17722</td>
</tr>
<tr>
<td>1.67</td>
<td>1.71264</td>
</tr>
<tr>
<td>1.55</td>
<td>1.55486</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measured d-spacings of platy hexagonal precipitates (Å)</th>
<th>d-spacings from ref. of kaolinite (Å)(^{58})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.72</td>
<td>3.70269</td>
</tr>
<tr>
<td>2.95</td>
<td>2.96199</td>
</tr>
<tr>
<td>1.93</td>
<td>1.9138</td>
</tr>
<tr>
<td>1.29</td>
<td>1.28681</td>
</tr>
</tbody>
</table>
Chapter 3. Na\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\) in Brines Affect CO\(_2\)–Brine–Biotite Interactions

Results of this chapter have been published in Environmental Science & Technology, 2013, 47 (1), 191 - 197.

Abstract

For sustainable geologic CO\(_2\) sequestration (GCS), a better understanding of the effects of brine cation compositions on mica dissolution, surface morphological change, and secondary mineral precipitation under saline hydrothermal conditions is needed. Batch dissolution experiments were conducted with biotite under conditions relevant to GCS sites (55–95°C and 102 atm CO\(_2\)). 1 M NaCl, 0.4 M MgCl\(_2\), or 0.4 M CaCl\(_2\) solutions were used to mimic different brine compositions, and deionized water was used for comparison. Faster ion exchange reactions (Na\(^+\)–K\(^+\), Mg\(^{2+}\)–K\(^+\), and Ca\(^{2+}\)–K\(^+\)) occurred in these salt solutions than in water (H\(^+\)–K\(^+\)). The ion exchange reactions affected bump, bulge, and crack formation on the biotite basal plane, as well as the release of biotite framework ions. In these salt solutions, numerous illite fibers precipitated after reaction for only 3 h at 95°C. Interestingly, in slow illite precipitation processes, oriented aggregation of hexagonal nanoparticles forming the fibrous illite was observed. These results provide new information for understanding scCO\(_2\)–brine–mica interactions in saline aquifers with different brine cation compositions, which can be useful for GCS as well as other subsurface projects.
3.1 Introduction

Deep saline aquifers are one of the most promising options for geologic CO$_2$ sequestration (GCS) because of their large storage capacity.$^{59,60}$ For safe and efficient GCS operation, it is important to understand how CO$_2$ injection-induced mineral dissolution and precipitation affect the aquifer’s porosity and permeability, which influence the caprock seal integrity and injectivity of CO$_2$. For example, in the Tensleep saline aquifer in Wyoming, the permeability of five core samples decreased by around 16–44% after CO$_2$ injection.$^{63}$ Therefore, we need a better understanding of scCO$_2$–brine–mineral interactions and the effect of environmental factors on these interactions.

In different deep saline aquifers, the brine cation compositions vary greatly.$^8,23,64,65$ Based on field site investigations, sodium is the most abundant cation in most deep saline waters,$^8,64,65$ constituting 70% to > 90% of total cations by mass.$^{64}$ Calcium is generally the second most abundant cation;$^8,64$ however, it could also be the most abundant cation in certain aquifers, and its concentration can be as high as 1.2 M.$^{64}$ In addition to Ca, there are also high concentrations of Mg.$^8,64$ For example, in Rose Sun sandstone, Ohio, the Mg concentration is 0.24 M.$^{65}$ The total electrolyte concentrations in brines can also vary greatly. For example, in the Michigan basin, Michigan, the salinity is over 400,000 mg/L, whereas at Silurian, Indiana, it is only 500 mg/L.$^8$ Hence, an improved understanding of cation effects on scCO$_2$–brine–mineral interactions is crucial.

Furthermore, maintaining caprock seal integrity is essential to prevent CO$_2$ leakage. Mica, a major component of caprock, is abundant at GCS sites.$^{22,23,66}$ The basal surface of micas usually carries a permanent negative charge,$^{67,68}$ where complexation, sorption, and ion-exchange
reactions with the cations in brines could occur. For different cations, their hydration states, water structures, and capacities for complexation, adsorption, and ion exchange reactions with the surfaces vary. Therefore, specific cations can play different roles in scCO₂–brine–mica interactions.

In our previous study in 1 M NaCl solution at 95°C and 102 atm CO₂, fast Na⁺–K⁺ ion exchange occurred, causing the fast release of biotite framework ions and biotite surface cracking, which induced numerous fibrous illite precipitation and its detachment from the biotite surface. This is particularly important considering the short reaction times and potential impacts on permeability changes if numerous illite fibers form in a reservoir. Different shapes of illite have been reported to differentially affect reservoir quality, such as permeability. However, how the abundant cations in brines affect scCO₂–brine–mica interactions under GCS conditions is unknown.

The objective of this study was to investigate the effect of abundant Na⁺, Mg²⁺, and Ca²⁺ in brines on mica alteration (i.e., dissolution, morphological evolution, and illite precipitation) under GCS conditions. Biotite was used as a model mica. Combining macroscopic fluid chemistry and microscopic surface analysis techniques, this study provides unique information on scCO₂–brine-mica interactions under GCS conditions.

3.2 Experimental Section

3.2.1 Chemicals and Minerals

All chemicals used were at least ACS grade. Ultrapure water (18.2 mΩ·cm at 25 °C) was used to prepare the salt solutions (1 M NaCl, 0.4 M MgCl₂, and 0.4 M CaCl₂ solutions). In
previous studies, significant effects of salinity on mica alteration have been reported; thus, the salt concentrations were chosen to have the same salinity and also to be relevant to GCS sites.

Biotite samples were obtained from Ward’s Natural Science, NY. The elemental compositions \([K_{0.91}Na_{0.08}(Mg_{0.52}Mn_{0.02}Fe_{0.37}Ti_{0.04})_3(Al_{1.00}Si_{3.00})O_{10}(F_{0.43}(OH)_{0.57})_2]\) characterized with both electron microprobe (EMP) and X-ray fluorescence (XRF) were in good agreement. Biotite crystals were cleaved to thin samples (~100 ± 20 µm) along the \([001]\) cleavage surface (basal plane), cut into 2.5 cm × 0.8 cm flakes, and cleaned.

3.2.2 High Pressure/Temperature Experiments, Analytical Methods, and Thermodynamic Calculations

A biotite flake and 4 mL of salt solution or deionized water (for comparison) were put in a PTFE tube inside the reactor (Parr Instrument Company, IL). Then the reactor was sealed and pressurized CO\(_2\) was injected. Batch experiments were conducted at 102 atm CO\(_2\) and 95°C for elapsed times of 3, 8, 17, 22, 44, 70, 96, 120, and 144 h. The pressure and temperature were chosen based on reported parameters for GCS sites, and they allowed obtaining experimental results within a reasonable time. A few experiments were conducted at lower temperatures (55, and 65°C) in 1 M NaCl solution, to investigate the effect of illite precipitation kinetics on its shape. To compare with the situation without CO\(_2\) injection, a 6 day batch experiment was also conducted at 102 atm N\(_2\) and 95°C in 1 M NaCl solution.

After reaction, the dissolved ion concentrations in solution were measured by inductively coupled plasma-mass spectrometry (ICP-MS, 7500ce, Agilent Technologies, CA). The reacted biotite basal surfaces were observed with atomic force microscopy (AFM, Nanoscope V Multimode SPM, Veeco). Both contact and tapping mode AFM were used. Contact mode was
used to scan larger surface areas, while tapping mode was used to scan smaller surface areas for recording more detailed morphology. To identify the mineral phase of the precipitates, the reacted biotite samples were sonicated for 30 min to detach the precipitates from the surface, and a drop of this suspension was placed on a Formvar/carbon-coated Cu grid. The electron diffraction patterns of the precipitates were measured using high resolution-transmission electron microscopy (HR-TEM, JEOL JEM-2100F field emission), to determine the atomic d-spacings of the precipitates.

Using Duan and Sun (2003)’s equations, we calculated the dissolved CO$_2$ concentrations at 102 atm and 95°C in different solutions. Using the dissolved CO$_2$ concentrations and the dissolved ion concentrations measured by ICP-MS, the cation activities and the pH values throughout the experiments were calculated using Geochemists’ Workbench (GWB, Release 8.0, RockWare, Inc.). Details of the sample preparation, experimental setup, AFM operation, and thermodynamic calculations are given in the Supporting Information.

### 3.3 Results and Discussion

#### 3.3.1 Ion Exchange Reactions and K$^+$ Release from Biotite

Preferential release of the biotite interlayer K$^+$ over the framework ions (Mg, Fe, Al, and Si) was observed in all solutions (Figures 3.1A–D), occurring through ion exchange reactions ($\text{Na}^+–\text{K}^+$, $\text{Mg}^{2+}–\text{K}^+$, $\text{Ca}^{2+}–\text{K}^+$, and $\text{H}^+–\text{K}^+$). Throughout the 6 day experiments, the released K concentrations in the salt solutions were $24 \pm 5$ times higher than in water (Figures 3.1A–D). Among the salt solutions, the released K concentrations were similar in the NaCl and MgCl$_2$ solutions, and slightly higher than in the CaCl$_2$ solution (Figures 3.1A–C).
Figure 3.1. Dissolved ion concentrations from biotite after reaction in 1 M NaCl (A), 0.4 M MgCl₂ (B), 0.4 M CaCl₂ (C), and deionized water (D) for different times at 102 atm CO₂ and 95°C. The concentrations are normalized by the stoichiometry of the biotite formula \([K_{0.91}Na_{0.08}(Mg_{0.52}Mn_{0.02}Fe_{0.37}Ti_{0.04})_3(Al_{1.00}Si_{3.00})O_{10}(F_{0.43}(OH)_{0.57})_2]\) to identify the dissolution congruency. For images A–C, the K concentrations are much higher than the framework ions (Mg, Fe, Al, and Si) and are read from the right y-axis.

The released K concentrations in these solutions can result from the ion exchange rates. Therefore, several mechanisms were considered as controlling the ion exchange rates. First, higher cation activities in the bulk solution can accelerate the ion exchange reactions, and cation activities in the bulk solution can be affected by both their activity coefficients and complexation with anions. Calculated with GWB (Table 3–S2 in Supporting Information), the H⁺, Na⁺, Mg²⁺, and Ca²⁺ activities were 0.0005, 0.60, 0.08, and 0.05 M in water, 1 M NaCl, 0.4 M MgCl₂, and 0.4 M CaCl₂ solutions, respectively. Based on these calculations, in water, the H⁺
activity (0.0005 M) was 2–3 orders of magnitude lower than the activities of other cations, which explained the much slower exchange in water (H⁺–K⁺) than in the salt solutions (Na⁺–K⁺, Mg²⁺–K⁺ and Ca²⁺–K⁺). Among the salt solutions, Mg²⁺ (0.08 M) and Ca²⁺ (0.05 M) activities were around 1 order of magnitude lower than that of Na⁺ (0.60 M). Considering the cation activity effect on the ion exchange rate, the Mg²⁺–K⁺ and Ca²⁺–K⁺ ion exchange should be much slower than the Na⁺–K⁺ ion exchange. However, the released K concentrations in these salt solutions were similar, thus, there must be other mechanisms affecting the ion exchange reactions.

Second, H⁺ can facilitate cation exchange with mica interlayer K⁺. However, GWB calculations (Table 3-S2 in the Supporting Information) showed that the pH values in different salt solutions were similar (the difference in pH values was within 0.34 throughout the 6 days experiment). Thus, the pH effect on ion exchange among these solutions is minor.

Third, the cation exchange reactions in these salt solutions were fast, and their rates were transport controlled instead of the surface reaction controlled. Thus, the local cation concentrations near the biotite surface should also be considered. Mica minerals carry negative charges, and thus attract cations to their surfaces. These adsorbed cations result in higher local cation concentrations near the surface than in the bulk. Different rates and orders of adsorption are known among the cations, depending on the surface potential, valence, and hydrodynamic radius. The order of cation preference by soil surfaces is known as the Lyotropic Series, where preferential adsorption of Mg²⁺ and Ca²⁺ over Na⁺ to mineral surfaces has been broadly reported, although the preference order between Mg²⁺ and Ca²⁺ varied among these reports. Therefore, more local Mg²⁺ and Ca²⁺ than Na⁺ are available to exchange with K⁺.

Based on the reasoning above, we summarized that Mg²⁺ and Ca²⁺ have lower activities in bulk solution; however, their higher surface preference over Na⁺ can cause high local Mg²⁺ and
Ca\(^{2+}\) concentrations near the biotite surface. Therefore, the opposing impacts can be offset causing the net aqueous K\(^+\) concentrations in all salt solutions to be similar.

3.3.2 Morphological Evolutions of Biotite Basal Surfaces and Relevance to Ion Exchange Reactions

Contact mode AFM analysis (Figures 3.2 and 3-S2) shows that the morphological changes of biotite basal surfaces after reaction are greatly influenced by different cations in brines. After reaction in the salt solutions for only 3 hrs, bumps and dendritic bulges formed on the biotite basal surfaces. Their abundance followed the order: CaCl\(_2\) > MgCl\(_2\) > NaCl (Figures 3.2A1, 3.2B1, and 3.2C1). After reaction for 8 hrs, cracks were first observed after reaction in CaCl\(_2\) (Figure 3.2C2). AFM observations have been conducted on mica basal surfaces after reaction in NaCl solution, and bump, bulge, and crack formation have been observed, which resulted from the swelling of the mica basal surface caused by Na\(^+\)–K\(^+\) ion exchange.\(^{23, 40, 69}\) The similar morphologies of bump, bulge, and crack formation on mica after reaction in CaCl\(_2\) and MgCl\(_2\) solutions observed here were also thought to be caused by cation exchange reactions.

Different swelling levels of mica caused by cation exchange have been previously reported by d-spacing measurement. With K\(^+\), Na\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\) as the interlayer cation, the d-spacings of phlogopite (magnesium mica) were reported to be 10.1, 12.3, 14.6, and 14.8 Å, respectively, and the H\(_2\)O contents in the samples as a weight percentage were <0.1%, 10.2%, 10.6%, and 11.9%, respectively.\(^{77}\) The order of swelling for cation exchange reactions agreed with the hydrated cation sizes: Ca\(^{2+}\) > Mg\(^{2+}\) > Na\(^+\).\(^{78, 79}\) Among the salt solutions, the released K concentrations were similar (Figure 3.1), while cracking occurred fastest after reaction with CaCl\(_2\) solution, and fewest bumps formed after reaction with NaCl solution. Based on our
observations of the swelling-induced morphology (bumps, bulges, and cracks) and the reported swelling effects and hydrated cation sizes, we suggest that when larger hydrated cations get into the biotite interlayer through ion exchange, more significant expansion of the biotite layer occurs, which could promote bump, bulge, and crack formation.

<table>
<thead>
<tr>
<th></th>
<th>3 hr</th>
<th>8 hr</th>
<th>22 hr</th>
<th>44 hr</th>
<th>4 days</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. 1 M NaCl</strong></td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>B. 0.4 M MgCl₂</strong></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>C. 0.4 M CaCl₂</strong></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
</tr>
</tbody>
</table>

**Figure 3.2.** Contact mode AFM observations of the biotite basal planes after reaction in 1 M NaCl (A), 0.4 M MgCl₂ (B), and 0.4 M CaCl₂ (C) at different elapsed reaction times at 102 atm CO₂ and 95°C. The AFM image size is 50 μm × 50 μm, and the height scale is 50 nm.

After reaction for 22 hrs, the biotite basal surfaces cracked in all these salt solutions (Figures 3.2A3, 3.2B3, and 3.2C3). Interestingly, as the reactions continued (44–144 hrs), after reaction with CaCl₂ (Figures 3.2C4–5) and MgCl₂ (Figures 3.2B4–5) solutions, numerous smaller cracks formed, with depths similar to the earlier ones (~10–20 nm throughout the 22–144 h reactions); while after reacting with NaCl solution, the depths of the cracks grew from 13.4 ± 5.0 to 57.5 ± 7.6 nm throughout the 22–70 h reaction (the surface after reaction for 44 h is shown in Figure 3.2A4). Disintegration of the biotite basal plane (Figure 3.2A5) and release of the surface
layer into solution also occurred. The mechanisms of different crack evolutions in the solutions are not clear at this moment, and are not the focus of this study.

In contrast, in water, the occurrence of bumps was rare, and neither bulges nor cracks were observed throughout the reaction period (Figure 3-S3 in Supporting Information). These differences can stem from the following reasons: First, the H⁺–K⁺ ion exchange was much slower than the ion exchange reactions in the salt solutions, as discussed in Section 3.1. Second, the hydrated H⁺ was much smaller than all the hydrated metal cations (Na⁺, Mg²⁺, and Ca²⁺), indicating that H⁺–K⁺ ion exchange causes much less swelling of the biotite layer than the ion exchange reactions in the salt solutions. Both mechanisms hindered bump, bulge, and crack formation in water.

3.3.3 Release of Biotite Framework Ions and Its Relevance to Ion Exchange Reactions and Morphological Changes

Throughout the experiments in water, the dissolved framework ion concentrations from biotite (Mg, Al, Si, and Fe) were around one order of magnitude lower than those in the salt solutions (Figure 3.1). In the salt solutions, faster ion exchange, more significant swelling, and more pronounced morphological changes were thought to have promoted the release of the framework ions.

Among the salt solutions, at the early stage of reaction (the shaded region in Figure 3.1), the dissolved framework ion concentrations followed the order: CaCl₂ > MgCl₂ > NaCl. Considering that this order agreed with that of the expansion caused by the different ion exchange reactions, and the pH and ionic strength values of the salt solutions were similar (Table 3-S2), we suggest that the release rates of the framework ions were controlled by the expansion caused by the ion
exchange reactions. The bigger the hydrated cation, the more significant the expansion and stress build up, which could weaken the bonds between the biotite framework ions with oxygen, promoting their release. In addition, in the CaCl₂ solution, the early crack formation after reaction for only 8 h (Figure 3.2C2) created more edge surface area of biotite in contact with solution, which further promoted the dissolution (Figure 3.1C). In the later stage, after reaction for 22 h in both 1 M NaCl and 0.4 M MgCl₂ solutions, the release rates accelerated (Figures 3.1A and 3.1B). The increased release rates were linked with the new edge surface areas generated through crack formation; After reaction for 96 h in 1 M NaCl solution, as discussed in our previous work,¹⁶⁹ the disintegration and detachment of the biotite surface layer further increased the biotite surface area in contact with solution, and thus further increased he framework ion release rates (Figure 3.1A).

3.3.4 Fibrous Illite Precipitation and Its Detachment from the Surface

In our previous study,¹⁶⁹ numerous illite fibers formed on the biotite surface after reaction in 1 M NaCl for only 3 h. In the current study, numerous fibrous precipitates were also observed on the biotite surface after reaction for 3 h in all three salt solutions (Figures 3.2A1, B1, and C1). They were confirmed to be illite, based on their fibrous shape, the characteristic 120°, and their diffraction patterns measured by HR-TEM (Figures 3.3A–C). However, in water, no macroscopic fibrous illite was observed throughout the experiments (Figure 3-S3).

To observe the details of the precipitates on the biotite surfaces, tapping mode AFM images were obtained. After reaction in 1 M NaCl at 95°C for 3 h (Figure 3.4A), the ends of the illite fibers (their growth directions) were observed as the oriented aggregates of nanoparticles. After reaction in DI water, hexagonal nanoparticles were observed on the biotite surface. Most of the nanoparticles were randomly distributed, but a few started to accumulate in a line, showing an
overall fibrous shape (Figure 3.4B). Interestingly, the hexagonal nanoparticles after reaction in water were also confirmed to be illite, based on their electron diffraction patterns measured by HRTEM (Figure 3.3D). To the best of our knowledge, this is the first time that direct nanoscale observations were made of the oriented aggregation of small hexagonal nanoparticles forming fibrous illite.

**Figure 3.3.** HRTEM results for secondary mineral phase identification after reaction of biotite in 1 M NaCl (A), 0.4 M MgCl\(_2\) (B), 0.4 M CaCl\(_2\) (C), and deionized water (D) at 102 atm CO\(_2\) and 95ºC. The insets are the electron diffraction patterns collected from the areas indicated by the arrows.
Figure 3.4. Tapping mode AFM observations of the biotite basal surface after reaction at 102 atm CO₂. The temperatures and solution compositions are shown in the figures. These amplitude mode images clearly show the morphology of the hexagonal nanoparticles. The height profiles below the AFM images are cut along the dashed lines in the corresponding AFM height mode images.

Both elongated–(such as fibrous) and platy–(such as hexagonal) shaped illite has been reported in both field site observations and laboratory illite synthesis (Table 3-S1 and Figure 3-S5). Fibrous-shaped illite can lower the permeability in porous media much more significantly than the platy–shaped illite.⁴³ Thus, a significant amount of research has been performed to study the mechanisms for the fibrous illite formation; however, there is no definite answer to this question yet. In recent decades, oriented aggregation has been widely observed for nanoparticle growth, such as TiO₂ and iron oxides nanoparticles.⁸⁰, ⁸¹ It was thought to be a non-classical growth mechanism that differed from Ostwald ripening.⁸², ⁸³ Based on our observations, we suggest that where slower illite formation kinetics occur, individual hexagonal nanoparticles
form and oriented aggregation occurs to form the fibrous shape. When faster illite formation kinetics occur, the illite quickly forms aggregations of small particles and grows as fibrous shapes. In water, the dissolved ion concentrations, especially K, were significantly lower than those in the salt solutions. Thus, much less illite formed, and during the slow illite precipitation, individual hexagonal particles precipitated, and some assembled as oriented aggregates to form the fibrous shape (Figure 3.4B). In the salt solutions, the fast ion release resulted in numerous illite precipitation; also, during this fast precipitation, the small illite particles aggregated fast and grew as fibrous shapes (Figure 3.4A). This hypothesis was further confirmed by AFM observations of the biotite surface after reaction in 1 M NaCl solution at 65°C. At this lower temperature, the dissolution and illite precipitation were slower than at 95°C, and the oriented aggregation of small hexagonal precipitates forming the fibrous shape was also observed (Figure 3.4C).

Throughout the experiments, bumps, bulges, and cracks on biotite surfaces were observed to control the amount of illite fibers on the biotite surface (Figure 3.2). During the early stage (3–17 h), their abundance on the biotite surface after reaction in the salt solutions followed the order: NaCl > MgCl₂ > CaCl₂, which is opposite to the trend of the abundance of bump, bulge, and crack formation (Figures 3.2A1–2, 3.2B1–2, and 3.2C1–2). In the later stage (22–144 h), when cracking of biotite surfaces occurred in all the salt solutions, the amount of fibrous illite on all the biotite surfaces diminished (Figures 3.2A3–5, 3.2B3–5, and 3.2C3–5). It is possible that when illite precipitated on the biotite surface, epitaxial interaction between illite and the biotite substrate occurred. Thus, when bumps, bulges, and cracks formed on the biotite surface, stress could build up in the bonds between the fibrous illite and the deformed biotite substrate, resulting
in the easy detachment of fibrous illite and the inhibition of the epitaxial illite formation on mica. The exact mechanism governing this phenomenon requires further investigation.

3.3.5 Enhanced Biotite Dissolution and Morphological Evolution by CO$_2$ Injection

Experiments conducted in 1 M NaCl for 6 days under 102 atm CO$_2$/N$_2$ were compared. The released biotite interlayer K concentration after reaction under N$_2$ for 6 days was only 60% of that under CO$_2$ (Table 3-S4). With CO$_2$ injection, the dissolved proton concentration was significantly higher, thus, the synergetic effect of protons on the cation exchange promoted the K release.$^{75}$ For the biotite framework ions, the released concentrations were more than 40 times higher after reaction under CO$_2$ than under N$_2$, indicating CO$_2$ injection at GCS sites will cause significantly enhanced mica dissolution.

In the experiment conducted in 1 M NaCl under N$_2$ gas for 6 days, bumps and fibrous illite were observed on the biotite surface, but no cracks appeared (Figure 3-S6) although the dissolved K concentration was 25% higher than those after reaction in 1 M NaCl under CO$_2$ for 22 h when cracks were already observed. Thus, the cracking formation is not related solely to cation exchange and K release. It could also be related to the release of biotite framework ions, or the presence of scCO$_2$, which might enhance crack formation.

3.4 Environmental Implications

In this study, using multidisciplinary techniques providing macroscopic aqueous chemistry and microscopic surface morphology analysis, we show that brine cation composition can control the ion exchange reactions with biotite interlayer K, as well as the resulting surface morphological evolutions and biotite framework ion release (Mg, Al, Fe, and Si). We observed
that the relative abundance of morphologies caused by swelling (such as bumps, bulges, and cracks) and that the early stage release rate of biotite framework ions followed the same order: CaCl$_2$ > MgCl$_2$ > NaCl >> water, which agreed with the order of the hydrated cation size$^{78, 79}$ and the expansion caused by the different ion exchange reactions.$^{77}$ Thus, we suggest that the larger hydrated cations can cause more stress on the biotite structure through ion exchange reaction, which can promote bump, bulge, and crack formation, as well as the release of the biotite framework ions.

Brine cation composition also affects the kinetics of illite precipitation as well as the resulting shape. During slow illite precipitation, the oriented aggregates of hexagonal nanoparticles forming the fibrous illite were directly observed for the first time. This observation suggests new possible mechanisms for fibrous illite formation. Precipitation of fibrous illite in sandstone pores has attracted much interest because the illite fibers can lower the permeability in porous media significantly and cause serious problems for hydrocarbon production.$^{43}$ Our observations provide insight for future work to improve the understanding of the fundamental mechanisms controlling the morphology of illite precipitates.

**Acknowledgments**

This work is supported by the NSF CAREER AWARD (EAR-1057117), and Y. Hu was partially supported by the Director, Office of Science, the Office of Basic Energy Sciences of the U.S. Department of Energy, in association with the Energy Research Frontier Center of Berkeley Lab, under Contract No. DE-AC02-05CH11231. We would like to acknowledge Dr. Ian Bourg for valuable discussion.
Supporting Information for Chapter 3

Contents: Four tables (3-S1 – 3-S4)

Six figures (3-S1 – 3-S6)

Figure 3-S1. Experimental setup for the high temperature and high pressure batch experiments. For the N₂ experiment, the syringe pump was connected with high purity N₂ cylinder.
1) Effect of Brine Composition on Morphology: Bumps, Bulges and Cracks

- 0.4 M MgCl$_2$
  - Bumps formed
  - Cracks go smaller

- 1 M NaCl
  - Cracks go deeper on the biotite basal surface in the presence of Na.
  - Cracks form after 17-22 h.

- 0.4 M CaCl$_2$
  - Lots of bumps formed on the biotite surface after 3 h.
  - Cracks and bulges form after 8 h.

Fibrous illite formed in all conditions, less formed in Ca, Mg cases.

**Figure 3-S2.** Additional contact mode AFM height images of biotite basal planes after reaction of single biotite flakes in different salt solutions (1 M NaCl, 0.4 M MgCl$_2$, or 0.4 M CaCl$_2$) under 102 atm CO$_2$ and 95°C for different times. The size of all the images is 50 μm, except for the image collected after reaction in 1 M NaCl solution for 70 h, in which the image size is 30 μm. The height scale for all the images is the same (50 nm).
**Figure 3-S3.** AFM contact mode height images of biotite basal plane after reaction in water under 102 atm CO\textsubscript{2} at 95ºC for 3, 8, 17, 44, 70, and 144 hrs. Bump formation was rare. No bulges, cracks or macroscopic fibrous illite were observed throughout the experiments. For all the images, the scan size is 50 μm, and the height scale is 50 nm.
Figure 3-S4. More tapping mode AFM images showing that aggregation of small particles forms the fibrous precipitates on the biotite basal plane after reaction under 102 atm CO₂ in 1 M NaCl solution at lower temperature (55°C). From the left to the right, height, amplitude, and phase images are shown.
Figure 3-S5. Illite crystallographic direction information for different shapes. Based on their aspect ratios (length/width), illite specimens can be categorized into two types: The first type is the platy shapes, such as lamellar, hexagonal or hexagonally related shapes. The second type is the elongated shapes such as laths and fibers which display aspect ratios ranging from 3 to 50 or more. Depending on their thicknesses, they can be rigid or flexible. Flexible laths are often referred to as ribbons; flexible fibers are referred to as filaments, whiskers, or hairs.
Figure 3-S6. AFM contact mode images of biotite basal plane after reaction in 1 M NaCl under 102 atm N$_2$ at 95ºC for 144 h. Bump and fibrous illite are observed, but no cracks. The scan size is 50 μm, and the height scale is 200 nm. From left to right, the images are in height, deflection error, and friction mode, respectively.
### Table 3-S1 Review of previous field and laboratory studies on illite morphology.

<table>
<thead>
<tr>
<th>Sample sites</th>
<th>Observations of illite shape</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permian Rotliegendes Sand, North Sea</td>
<td>The diagenetic growth of fibrous illite in sandstone reservoirs was first documented: the illite develops long, lath-like projections, which are commonly curled and up to 30 μm long. These lath-like growths bridge the gap between the adjacent detrital sand grains.</td>
<td>84</td>
</tr>
<tr>
<td>St Peter Sandstone, Missouri</td>
<td>Illite grown from the edges of a kaolinite, ranging in length from 1 to 10 μm, and appearing in sets of parallel fibers growing from an euhedral kaolinite platelet. Single, double, and triple sets of illite fibers, which have an angle of 120° between fibers, are common.</td>
<td>36</td>
</tr>
<tr>
<td>Rhourde El Baguel Sandstone, Eastern Sahara</td>
<td>Illite laths range in length from 0.3 to 30 μm and show a radial growth from a core in bundles. Some of the illite clusters intersect at 120°. They can grow both at the edges of a core mica and epitaxially on the basal plane of mica.</td>
<td>36</td>
</tr>
<tr>
<td>Multiple core samples, Eastern Paris Basin</td>
<td>Both lath- and hexagonal illites were observed. With increasing depth, sizes of illite in both shapes increased, and the ratio of the lath-shaped illite decreased.</td>
<td>85</td>
</tr>
<tr>
<td>Lower Permian Rotliegend sandstone reservoir, Germany</td>
<td>Illite minerals typically are present either as aggregates of monocrystalline euhedral crystals as replacements of pore-filling kaolin aggregates, or as 5–15 μm thick coatings on the surfaces of the framework quartz grains as pore-lining. In wells showing intense illitization, these coatings are often two-layered, with a compact inner layer and an outer layer composed of laths growing radially into the pores and filling intergranular voids as pore-bridging. In the shallow well, illite samples are very elongated, filamentous, and hairy. With increasing burial depth, their shapes changed to a more rigid lath, and then were pseudo-hexagonal-shaped.</td>
<td>86</td>
</tr>
</tbody>
</table>

### Illite laboratory syntheses

<table>
<thead>
<tr>
<th>Materials for synthesis</th>
<th>Experimental conditions</th>
<th>Observations of illite shape</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite powder in KCl solution</td>
<td>200°C, 500 bar, for 24–84 days, neutral pH</td>
<td>First attempt to synthesize fibrous illite; negligible quantities of fibrous illite, large amounts of lamellar (platy) illite formation were reported.</td>
<td>87</td>
</tr>
<tr>
<td>Amorphous Al/Si gels in chloride, oxalate solutions</td>
<td>150–350°C, 750–1000 bar,</td>
<td>Fibrous/lath-type illite formed during the fast illite precipitation in the presence of oxalate, while platy illite formed during the slow precipitation in the absence of oxalate.</td>
<td>88</td>
</tr>
<tr>
<td>Kaolinite, KOH</td>
<td>35 and 80°C, up to 4 years</td>
<td>Both platy and lath-shaped illites were synthesized in the absence of organic acids. Laths appeared at lower supersaturation with respect to illite formation and relatively slower growth rate than the platy illite formation. Laths were eventually recrystallized to platy illites.</td>
<td>89</td>
</tr>
</tbody>
</table>
Table 3-S2. GWB calculations of the solution conditions conducted at 102 atm CO$_2$ and 95$^\circ$C

<table>
<thead>
<tr>
<th>Solution</th>
<th>1 M NaCl</th>
<th>0.4 M MgCl$_2$</th>
<th>0.4 M CaCl$_2$</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major cation</td>
<td>Na$^+$</td>
<td>Mg$^{2+}$</td>
<td>Ca$^{2+}$</td>
<td>H$^+$</td>
</tr>
<tr>
<td>CO$_2$ Solubility (mol/kg water)</td>
<td>0.68</td>
<td>0.72</td>
<td>0.72</td>
<td>0.82</td>
</tr>
<tr>
<td>pH (initial–6 days)</td>
<td>3.22–3.77</td>
<td>3.02–3.43</td>
<td>3.00–3.44</td>
<td>3.25–3.32</td>
</tr>
<tr>
<td>Ionic strength (M)</td>
<td>1.05</td>
<td>1.13</td>
<td>1.06</td>
<td>0.0006–0.0008</td>
</tr>
<tr>
<td>Free cation concentration (M)$^1$</td>
<td>0.97</td>
<td>0.33</td>
<td>0.30</td>
<td>0.0005</td>
</tr>
<tr>
<td>Activity coefficient for the cations</td>
<td>0.62</td>
<td>0.26</td>
<td>0.18</td>
<td>0.97</td>
</tr>
<tr>
<td>Free cation activity (M)$^2$</td>
<td>0.60</td>
<td>0.08</td>
<td>0.05</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

$^1$The free cation concentration listed in the table is the concentration of the cation not forming complexes with the anions. It equals the total cation concentration minus the concentrations of the cation complexes. For example, the listed Ca$^{2+}$ concentration equals the total Ca concentration (0.4 M) minus the concentration of CaCl$^+$ and CaHCO$_3^+$.

$^2$The free cation concentration multiplied by its activity coefficient gives the free cation activity.
Table 3-S3. The d-spacings of illite reference match well with the HR-TEM measured d-spacings of the fibrous precipitates formed after reaction in 1 M NaCl (Figure 3A), 0.4 M MgCl₂ (Figure 3B), 0.4 M CaCl₂ solutions (Figure 3C), and the hexagonal precipitates formed after reaction in H₂O (Figure 3D).

A. After reaction in 1 M NaCl

<table>
<thead>
<tr>
<th>Measured d-spacing (Å)</th>
<th>d-spacing from ref. of illite (Å)</th>
<th>Crystal plane</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.03</td>
<td>10.02</td>
<td>(0 0 2)</td>
<td>62.3%</td>
</tr>
<tr>
<td>3.86</td>
<td>3.9115</td>
<td>(1 1 -3)</td>
<td>27.4%</td>
</tr>
<tr>
<td>3.14</td>
<td>3.1300</td>
<td>(1 1 -5)</td>
<td>31.4%</td>
</tr>
<tr>
<td>2.39</td>
<td>2.3800</td>
<td>(1 3 3)</td>
<td>29.5%</td>
</tr>
<tr>
<td>2.09</td>
<td>2.0800</td>
<td>(2 2 3)</td>
<td>10.4%</td>
</tr>
<tr>
<td>1.43</td>
<td>1.4439</td>
<td>(1 5 7)</td>
<td>1.7%</td>
</tr>
</tbody>
</table>

B. After reaction in 0.4 M MgCl₂

<table>
<thead>
<tr>
<th>Measured d-spacing (Å)</th>
<th>d-spacing from ref. of illite (Å)</th>
<th>Crystal plane</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.48</td>
<td>4.47603</td>
<td>(1 1 -1)</td>
<td>100.0%</td>
</tr>
<tr>
<td>3.58</td>
<td>3.50154</td>
<td>(1 1 -4)</td>
<td>60.5%</td>
</tr>
<tr>
<td>2.64</td>
<td>2.59694</td>
<td>(1 3 -1)</td>
<td>57.3%</td>
</tr>
<tr>
<td>2.28</td>
<td>2.38522</td>
<td>(1 3 3)</td>
<td>29.5%</td>
</tr>
<tr>
<td>1.76</td>
<td>1.75077</td>
<td>(2 2 -8)</td>
<td>3.3%</td>
</tr>
<tr>
<td>1.52</td>
<td>1.52856</td>
<td>(1 3 -11)</td>
<td>13.4%</td>
</tr>
</tbody>
</table>
### C. After reaction in 0.4 M CaCl₂

<table>
<thead>
<tr>
<th>Measured d-spacing (Å)</th>
<th>d-spacing from ref. of illite (Å)</th>
<th>Crystal plane</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.48</td>
<td>4.47603</td>
<td>(1 1 -1)</td>
<td>100.0%</td>
</tr>
<tr>
<td>3.58</td>
<td>3.50154</td>
<td>(1 1 -4)</td>
<td>60.5%</td>
</tr>
<tr>
<td>2.57</td>
<td>2.59694</td>
<td>(1 3 -1)</td>
<td>57.3%</td>
</tr>
<tr>
<td>2.28</td>
<td>2.38522</td>
<td>(1 3 3)</td>
<td>29.5%</td>
</tr>
<tr>
<td>1.67</td>
<td>1.75077</td>
<td>(2 2 -8)</td>
<td>3.3%</td>
</tr>
<tr>
<td>1.48</td>
<td>1.52856</td>
<td>(1 3 -11)</td>
<td>13.4%</td>
</tr>
</tbody>
</table>

### D. After reaction in H₂O

<table>
<thead>
<tr>
<th>Measured d-spacing (Å)</th>
<th>d-spacing from ref. of illite (Å)</th>
<th>Crystal plane</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.56</td>
<td>4.47603</td>
<td>(1 1 -1)</td>
<td>100.0%</td>
</tr>
<tr>
<td>3.58</td>
<td>3.50154</td>
<td>(1 1 -4)</td>
<td>60.5%</td>
</tr>
<tr>
<td>2.64</td>
<td>2.59694</td>
<td>(1 3 -1)</td>
<td>57.3%</td>
</tr>
<tr>
<td>2.28</td>
<td>2.38522</td>
<td>(1 3 3)</td>
<td>29.5%</td>
</tr>
<tr>
<td>1.72</td>
<td>1.75077</td>
<td>(2 2 -8)</td>
<td>3.3%</td>
</tr>
<tr>
<td>1.56</td>
<td>1.52856</td>
<td>(1 3 -11)</td>
<td>13.4%</td>
</tr>
</tbody>
</table>
Table 3-S4. Comparison of the dissolved ion concentrations (μM, mean ± standard deviation) from biotite after reaction for 6 days in 1 M NaCl solution under 102 atm CO₂ or N₂ at 95°C. The concentrations are normalized by the stoichiometry of the biotite formula \([K_{0.91}Na_{0.08}(Mg_{0.52}Mn_{0.02}Fe_{0.37}Ti_{0.04})_{3}(Al_{1.00}Si_{3.00})O_{10}(F_{0.43}(OH)_{0.57})_2]\).

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>244 ± 9.7</td>
<td>218 ± 9.5</td>
<td>268 ± 10.0</td>
<td>1166 ± 80.5</td>
<td>219 ± 10.3</td>
</tr>
<tr>
<td>N₂</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>700 ± 50.5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

Note: All the solutions were diluted 30 times before ICP-MS analysis, to lower the dissolved salt concentration (1 M NaCl), which can cause damage to the instrument. After reaction under N₂, the normalized dissolved framework ion concentrations (Mg, Al, Si, and Fe) were below 5 μM, and are thus more than 40 times lower than those released after reaction under CO₂.
Chapter 4. Biotite Dissolution in Brine: Its Activation Energy and CO₂ Intercalation

Results of this chapter have been published in Langmuir, 2012, 28 (41):14633-14641.

Abstract

For sustainable geologic CO₂ sequestration (GCS), it is important to understand the effects of temperature and CO₂ pressure on mica’s dissolution and surface morphological changes under saline hydrothermal conditions. Batch experiments were conducted with biotite (Fe-end member mica) under conditions relevant to GCS sites (35–95 °C and 75–120 atm CO₂), and 1 M NaCl solution was used to mimic the brine. With increasing temperature, a transition from incongruent to congruent dissolution of biotite was observed. The dissolution activation energy based on Si release was calculated to be 52 ± 5 kJ mol⁻¹. By comparison with N₂ experiments, we showed that CO₂ injection greatly enhanced biotite’s dissolution and its surface morphology evolutions, such as crack formation and detachment of newly formed fibrous illite. For biotite’s dissolution and morphological evolutions, the pH effects of CO₂ were differentiated from the effects of bicarbonate complexation and CO₂ intercalation. Bicarbonate complexation effects on ion release from biotite were found to be minor under our experimental conditions. On the other hand, the CO₂ molecules in brine could get into the biotite interlayer and cause enhanced swelling of the biotite interlayer and hence the observed promotion of biotite surface cracking. The cracking created more reactive surface area in contact with brine and thus enhanced the later
ion release from biotite. These results provide new information for understanding CO₂–brine–mica interactions in saline aquifers with varied temperatures and CO₂ pressures, which can be useful for GCS site selection and operations.
4.1 Introduction

Because of their large storage capacity, deep saline aquifers are a promising option for long-term geologic CO$_2$ sequestration (GCS). Maintaining high injectivity of the storage formation and good seal integrity of the caprock are essential for efficient and safe GCS. Lowering the porosity and permeability of the storage formation will lower the CO$_2$ injectivity and its storage capacity, while increasing the porosity and permeability of the caprock may lead to potential CO$_2$ leakage. Geochemical reactions can affect the physical, mechanical, and hydrological properties of reservoirs, such as their porosity, fracture aperture, permeability, and capillary pressure, and thus alter the CO$_2$ injectivity and the seal integrity of caprock. Therefore, for safer and more efficient GCS operation, it is important to understand injected CO$_2$-induced mineral dissolution and precipitation under relevant GCS conditions.

Mica, as a clay mineral, is a major component of caprock abundant at GCS sites. The importance of clay minerals in controlling permeability and caprock integrity during CO$_2$ injection has been broadly reported. However, compared with feldspar and carbonate, fewer studies have been conducted on CO$_2$–brine–mica interactions under GCS conditions. In our previous study, we conducted experiments with biotite (Fe-end member mica), as a model clay mineral, in 1 M NaCl solution at 95 °C and 102 atm CO$_2$. Numerous illite fibers precipitated on the biotite surface after reaction for only 3 h, and biotite surface cracking and resulting fibrous illite detachment occurred after reaction for only 22 hours. The biotite surface cracking and fibrous illite mobilization are important. Clay mobilization during freshwater flooding has been broadly reported to have caused permeability decrease of saline aquifers, and fibrous illite formation has also been reported to decrease aquifer permeability greatly.
Thus, during CO₂ injection, the fast formation and mobilization of fibrous illite through CO₂–brine–biotite interactions could cause significant changes in aquifer permeability within relatively short time frames.

At different GCS field sites, temperature and CO₂ pressure vary greatly with injection depth (Table 4-S1 in the Supporting Information (SI)). Temperature has been broadly reported to affect CO₂ solubility, and mineral dissolution/precipitation kinetics and mechanisms. Dissolution activation energy, which characterizes mineral dissolution rate as a function of temperature, is important for geochemical modeling. To calculate the activation energy of biotite dissolution ($E_a$), Palandri and Kharaka compiled the biotite dissolution data obtained by different researchers and derived an $E_a$ value of 22 kJ mol$^{-1}$.

Mcmaster et al. did high resolution imaging of biotite dissolution using tapping-mode atomic force microscopy (AFM), and calculated an $E_a$ value of 49 kJ mol$^{-1}$ over the temperature range of 10–35 °C, which is cooler than common GCS conditions. In addition to temperature, the pressure of CO₂ could affect the dissolved aqueous CO₂ concentration, changing the pH of the saline brine and the dissolved bicarbonate concentration. Several researchers have shown the effects of bicarbonate complexation on the dissolution stoichiometry and kinetics of aluminosilicates. All of these previous studies showed the potential effects of temperature and CO₂ pressure on CO₂–brine–mica interactions; however, none of them were conducted under relevant GCS conditions of high temperature, high CO₂ pressure, and high salinity.

The objective of this study was to investigate the effects of temperature and CO₂ pressure on mica alteration (i.e., mica dissolution and morphological evolution, such as crack formation and illite precipitation and its mobilization) under GCS conditions. Biotite was used as a model mica. The activation energy of biotite dissolution under relevant GCS conditions over the temperature
range of 35–95 °C was calculated. For biotite dissolution and morphological evolution, the pH effects of CO$_2$ were differentiated from the effects of bicarbonate complexation and CO$_2$ intercalation. The unique information of the temperature and CO$_2$ pressure effects on CO$_2$–brine–mica interactions provided here can guide GCS site selection and safer operation.

4.2 Experimental Section

4.2.1 Chemicals and Minerals

All chemicals used were at least ACS grade. Ultrapure water (18.2 mΩ·cm at 25 °C) was used to prepare the solutions. Biotite samples were obtained from Ward’s Natural Science, NY, and then characterized as [K$_{0.91}$Na$_{0.08}$Mg$_{0.52}$Mn$_{0.02}$Fe$_{0.37}$Ti$_{0.04}$]$_3$(Al$_{1.00}$Si$_{3.00}$)O$_{10}$[F$_{0.43}$(OH)$_{0.57}$]$_2$ via electron microprobe (EMP). Biotite crystals were cleaved to thin samples (~100 ± 20 µm) along the {001} cleavage surface (basal plane), then cut into 2.5 cm × 0.8 cm flakes. The mass of a single flake was 0.015 ± 0.003 g.

4.2.2 High Pressure/Temperature Experimental Design and Setups, Analytical Methods, and Thermodynamic Calculations

Experimental design. Four sets of batch experiments were conducted. In set (1), to investigate the temperature effects and calculate the activation energy of biotite dissolution, batch experiments were conducted in 1 M NaCl solution under 102 atm CO$_2$ at 35, 55, 75, and 95 °C for elapsed times of 3, 22, 44, and 70 h. In set (2), to study the injected CO$_2$-induced effects, batch experiments were conducted in 1 M NaCl solution under 102 atm N$_2$ at 95 °C to simulate the condition before CO$_2$ injection. In set (3), to differentiate the pH effects from other effects induced by high CO$_2$ pressure, experiments were conducted under 102 atm N$_2$ at 95 °C in 1 M
NaCl solution, with pH adjusted by HCl. Batch experiments of sets (2) and (3) were conducted for elapsed times of 3, 22, 44, 70, and 144 h. In set (4), to study the effects of different CO₂ pressures under relevant GCS conditions, experiments were conducted for 22 h at both low (35 °C) and high (95 °C) temperatures at 75, 102, and 120 atm of CO₂ pressure.

Experimental setups. A mini benchtop reactor, made of Hastelloy C (Parr Company, IL), was connected to a syringe pump (Teledyne ISCO, Lincoln, NE) to conduct experiments at controlled temperatures and pressures. For the four sets of batch experiments, a biotite flake and 4 ml 1 M NaCl solution (with HCl added in set (3)) were put in a Teflon tube inside the reactor. A relatively low biotite/brine ratio (3.75 mg/ml) was used to avoid significant precipitation, which can affect the measured dissolved ion concentrations in reacted brines. After that, the reactor was sealed, purged with CO₂ or N₂ for 20 minutes to remove the air inside the reactor. Then, pressurized CO₂ or N₂ was injected and batch experiments were conducted at constant temperatures and pressures.

For in situ pH measurements, we used special pH probes (Corr Instrument, TX) operating at 95 °C under 102 atm CO₂ or 102 atm N₂ with HCl added. The probes were placed inside the Teflon lined reactor, and 20 pieces of biotite flakes in 80 mL solution were added. This was the same rock/solution ratio as the batch experiments. The experimental setups for the batch reactions and in situ pH measurements are shown in Figures 4-S1, 4-S2 in the SI, respectively.

Analytical Methods. After reaction, the dissolved ion concentrations in solutions were measured by inductively coupled plasma-mass spectrometry (ICP-MS, 7500ce, Agilent Technologies, CA). The reacted biotite basal surfaces were observed with contact mode atomic force microscopy (AFM, Nanoscope V Multimode SPM, Veeco). To identify the mineral phases
of the precipitates, the reacted biotite samples were sonicated for 30 min to detach the precipitates from the surface, and a drop of this suspension was placed on a Formvar/carbon-coated Cu grid. The electron diffraction patterns of the precipitates were measured using high resolution-transmission electron microscopy (HR-TEM, JEOL JEM-2100F field emission), and the atomic d-spacings of the precipitates were calculated to determine their mineral phases.

Thermodynamic Calculations. The salinity, pH values, and dissolved aqueous CO$_2$ and bicarbonate activities in 1 M NaCl solutions under different CO$_2$ pressures and temperatures were calculated with Geochemists’ Workbench (GWB, Release 8.0, RockWare, Inc.). The amount of HCl added was also calculated using GWB to make the initial 1 M NaCl solution under 102 atm N$_2$ have the same pH as the solution under 102 atm CO$_2$ at 95 ºC. Details of the experimental operations including in situ pH measurements and AFM operations, and thermodynamic calculations can be found in the SI of our previous publications.$^{69,106}$

4.3 Results and Discussion

4.3.1 Effects of Temperature on Biotite Surface Cracking and Dissolution Congruency: Calculations of Dissolution Activation Energy

Contact mode AFM analysis shows that numerous fibrous precipitates form on the biotite basal surfaces after reaction for 3 h over the temperature range of 35–95 ºC (Figure 4.1). The d-spacings of the precipitates measured by electron diffraction with HR-TEM matched well with those of the illite references (Table 4-S2). Based on their morphology and electron diffraction results, these precipitates were confirmed to be illite.$^{69}$ As reaction went on, more significant morphological evolutions of biotite basal surfaces occurred at higher temperatures (Figure 4.1). After reaction at 95 ºC for only 22 hrs, the biotite basal surfaces cracked (Figure 4.1A2) and illite
detached from the cracked surface. Cracks started to be observed after reaction at 75 °C (Figure 4.1B) for 70 h, but cracking did not occur within 70 h after reaction at 55 °C (Figure 4.1C) and 35 °C (Figure 4.1D).

Figure 4.1. Height mode AFM images of biotite basal planes after reaction in 1 M NaCl solution under 102 atm CO₂ at 95 °C (A), 75 °C (B), 55 °C (C), and 35 °C (D) for different elapsed reaction times. The AFM image size is 50 μm × 50 μm, except for image A4, which is 30 μm × 30 μm.

Dissolved ion concentrations after reaction under 35–95 °C were normalized according to their stoichiometry in the biotite structure, and are shown in Figure 4.2. Preferential release of the biotite interlayer K⁺ over the framework ions (Mg, Fe, Al, and Si) was observed over the temperature range (Figure 4.2), occurring through fast ion exchange reaction (Na⁺–K⁺). The overall interlayer ion release rates of the fast ion exchange reactions were generally transport-
controlled instead of surface reaction-controlled. This is confirmed by the parabolic curve shapes of the released K concentrations over reaction time (Figure 4.2).

![Graphs showing dissolution of biotite](image)

**Figure 4.2.** Dissolved ion concentrations from biotite after reaction in 1 M NaCl solution under 102 atm CO₂ at 95 ºC (A), 75 ºC (B), 55 ºC (C), and 35 ºC (D) for different elapsed reaction times. The concentrations are normalized by the stoichiometry of the biotite formula \([K_{0.91}Na_{0.08}(Mg_{0.52}Mn_{0.02}Fe_{0.37}Ti_{0.04})_3(Al_{1.00}Si_{3.00})O_{10}(F_{0.43}(OH)_{0.57})_2]\) to identify the dissolution congruency. The K concentrations are much higher than the framework ions (Mg, Fe, Al, and Si) and are divided by a factor of 10 (A and B) or 20 (C and D).

During the first 70 h of reactions at 95 ºC and 75 ºC (Figures 4.2A and 4.2B), the releases of all framework ions (Mg, Al, Si, and Fe) were congruent. While within 70 h, in reactions at 55 ºC and 35 ºC (Figures 4.2C and 4.2D), the release of Mg, Al, and Fe were preferential over Si. For
biotite dissolution at room temperature in acidic pH, the preferential release of Mg, Al, and Fe over Si have been broadly reported: Kalinowski and Schweda conducted experiments with biotite powders at 22 °C under pH 1–4 conditions, and the release of the framework ions followed the order Mg, Fe, Al > Si.\textsuperscript{19} Preferential release of Mg, Fe, and Al over Si was also observed after reaction of biotite single crystals at 24 °C and pH 1.\textsuperscript{41} Acker and Bricker reported that the release rates of framework ions from biotite at 22 °C and pH 3 followed the order Mg, Fe > Al, Si.\textsuperscript{56} From low to high temperature, evolution from incongruent to congruent dissolution has been reported for albite\textsuperscript{107} and labradorite,\textsuperscript{108} but not yet for biotite. In our study, from low to high temperature under acidic pH conditions, the transition from preferential dissolution of Mg, Al, and Fe over Si to congruent dissolution of biotite framework ions was directly observed for the first time.

To calculate the activation energy (E\textsubscript{a}) of biotite dissolution, we need to know the Si release rates, as the rate-determining step of biotite dissolution, at different temperatures. Before crack formation, all biotite flake samples at different temperatures had the same surface areas in contact with solution. Thus, we could compare the ion release rates by comparing the dissolved ion concentrations without surface area normalization. After reaction at 95 °C, before crack formation (22 h), a fairly good linear relationship between the released Si concentrations and the reaction times was observed (Figure 4.2A, R\textsuperscript{2} = 0.99). Within 70 h in reactions at 35, 55, and 75 °C, good linear fittings of the released Si concentrations over reaction times were also obtained (Figures 4.2B, 4.2C, and 4.2D, R\textsuperscript{2} > 0.95). Thus, the Si release rates at 35, 55, 75, and 95 °C were obtained from the slopes of the linear fittings (Figure 4.2). Then, the activation energy (E\textsubscript{a}) of biotite dissolution was calculated to be 52 ± 5 kJ mol\textsuperscript{-1} (= 12 kcal mol\textsuperscript{-1}), using the Arrhenius equation (Figure 4-S3). Aqueous diffusion-controlled reactions typically have activation energies
that are less than 5 kcal mol\(^{-1}\). Thus, according to the calculated activation energy, biotite dissolution, based on Si release rate, was surface reaction-controlled instead of transport-controlled. The activation energy of biotite dissolution over the low temperature range of 10–35 °C without scCO\(_2\) was reported to be 49 ± 2 kJ mol\(^{-1}\), which is quite similar to the value we calculated here at high temperatures under a high pressure of scCO\(_2\). In Garcia et al.’s research, the activation energy of phlogopite (Mg-end member mica) dissolution, based on Si release under similar GCS conditions (in 1 M NaCl, 75–95 °C, under 75 atm scCO\(_2\) with solution pH around 3), was reported to be 64.2 kJ mol\(^{-1}\). The activation energy of Si release from phlogopite is higher than from biotite dissolution, indicating that it is harder to break the Si–O bonds in phlogopite than in biotite under these conditions, which agreed with the broadly reported fact that the dissolution of biotite is faster than phlogopite under acidic pH conditions. The activation energy value for biotite dissolution under relevant GCS conditions we provide here can be used in the geochemical modeling of reactive transport simulations, to more accurately predict the fate and transport of injected CO\(_2\) at GCS sites.

4.3.2 Differentiation of the pH Effects of CO\(_2\) from the Effects of Bicarbonate Complexation and CO\(_2\) Intercalation

To study the effects of CO\(_2\) injection on CO\(_2\)–brine–biotite interactions, we compared the morphological evolutions of the biotite basal surfaces after reaction in 1 M NaCl under 102 atm CO\(_2\) (initial pH = 3.1, calculated by GWB) and N\(_2\) (initial pH = 6.1, calculated by GWB) at 95 °C. As shown in Figures 4.1A and 4.3A, CO\(_2\) injection caused cracking of the biotite basal surface within 22 h, while no cracking occurred throughout the 6 day experiments with N\(_2\). The dissolved ion concentrations after reaction under CO\(_2\) and N\(_2\) are shown in Figures 4.2A and 4.4A,
respectively. CO$_2$ injection was found to greatly enhance the release of biotite framework ions (by a factor of more than 40 at the end of the 6 day experiments), and to promote the release of interlayer K (by a factor of ~1.5 throughout the 6 day experiments).

<table>
<thead>
<tr>
<th></th>
<th>3 hr</th>
<th>22 hr</th>
<th>44 hr</th>
<th>70 hr</th>
<th>6 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. 95 °C, N$_2$</td>
<td>A1</td>
<td>A2</td>
<td>A3</td>
<td>A4</td>
<td>A5</td>
</tr>
<tr>
<td>pH$_{initial}$ = 6.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B. 95 °C, N$_2$ + HCl</td>
<td>B1</td>
<td>B2</td>
<td>B3</td>
<td>B4</td>
<td>B5</td>
</tr>
<tr>
<td>pH$_{initial}$ = 3.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.3.** Figures A and B show height mode AFM images of biotite basal planes after reaction in 1 M NaCl solution at 95 °C under 102 atm N$_2$ (A) and 102 atm N$_2$ with HCl added (B). The AFM image size is 50 μm × 50 μm.

During and after CO$_2$ injection, several possible mechanisms could contribute to enhanced biotite dissolution and surface morphological changes: First, CO$_2$ injection can acidify the originally circum-neutral brine: faster biotite dissolution under acidic pH conditions than neutral pH has been reported$^{56, 110}$ and this faster dissolution can also promote the surface morphological evolutions. Second, CO$_2$ injection will increase the dissolved bicarbonate concentrations in brine. The effect of bicarbonate on clay dissolution has not yet been extensively studied. Based on previous studies, the main effect of bicarbonate on aluminosilicate dissolution would be forming complexes with the mineral surfaces as well as aqueous cations, thus affecting the ion release rates$^{103-105}$. Third, CO$_2$ injection will increase the concentrations of CO$_2$ molecules in brine. The reported main interactions of CO$_2$ molecules with clays were
adsorption to the external surfaces of clays and intercalation into clay interlayers. The intercalation has been reported to cause clay to swell.\textsuperscript{111-113}

**Figure 4.4.** Figures A and B show the released ion concentrations from biotite after reaction in 1 M NaCl solution at 95 °C under 102 atm N\textsubscript{2} (A) and 102 atm N\textsubscript{2} with HCl added (B). The concentrations are normalized by the stoichiometry of the biotite formula [K\textsubscript{0.91}Na\textsubscript{0.08}(Mg\textsubscript{0.52}Mn\textsubscript{0.02}Fe\textsubscript{0.37}Ti\textsubscript{0.04})\textsubscript{3}(Al\textsubscript{1.00}Si\textsubscript{3.00})O\textsubscript{10}(F\textsubscript{0.43}(OH)\textsubscript{0.57})\textsubscript{2}] to identify the dissolution congruency. The K concentrations are much higher than the framework ions (Mg, Fe, Al, and Si) and are divided by a factor of 10.

To delineate the pH effects from other CO\textsubscript{2} injection-induced effects described above, we compared experiments conducted under 102 atm CO\textsubscript{2} and under 102 atm N\textsubscript{2}, with pH adjustment using HCl. This GWB calculation was confirmed by \textit{in situ} pH measurements, which showed that the pH values for the two cases were the same within 44 h reaction time (Figure 4-S4). After reaction for 70 and 144 h, the pH values under N\textsubscript{2} with HCl adjustment were around 0.2 and 0.3 units higher than those after reaction under CO\textsubscript{2} (Figure 4-S4). As biotite dissolves with time (eqn. (1) and (2); the stoichiometries of the chemical species are not balanced in eqn. (2)), cations are released from biotite with the consumption of protons from the solution, increasing the solution pH values. For the CO\textsubscript{2} case, the consumption of protons in solution promotes the dissociation of the dissolved carbonic acid (eqn. (3)), which provides protons in the solution. For
the N₂ with HCl case, HCl acid does not have such a buffer effect as carbonic acid. Thus, after reaction for a longer time, the pH values in the N₂ with HCl case increased further than in the CO₂ case.

\[
K(Mg,Fe)_3AlSi_3O_{10}(OH, F)_2 + Na^+ \rightarrow Na(Mg,Fe)_3AlSi_3O_{10}(OH, F)_2 + K^+, \tag{1}
\]

\[
Na(Mg,Fe)_3AlSi_3O_{10}(OH, F)_2 + H^+ \rightarrow Na^+ + Mg^{2+} + Fe^{2+} + Fe^{3+} + Al^{3+} + Si^{4+} + F^- + H_2O, \tag{2}
\]

\[
CO_2(aq) + H_2O \rightarrow H^+ + HCO_3^-. \tag{3}
\]

The biotite surface morphological evolutions in the two cases are shown in Figures 4.1A and 4.3B. For both cases, numerous fibrous precipitates formed on the biotite basal surfaces after reaction for 3 h. These precipitates were confirmed to be illite, based on their morphology and their d-spacing matching with illite.\(^6^9\) Interestingly, after reaction for longer times, much more significant surface morphological evolutions occurred in the CO₂ case (Figure 4.1A) than in the N₂ with HCl case (Figure 4.3B). For the CO₂ case, many cracks were observed on the biotite surface after only 22 h reaction (Figure 4.1A2). However, for the N₂ with HCl case, cracks were not observed until 70 h reaction time (Figure 4.3B).

The dissolved ion concentrations for these two cases are shown in Figures 4.2A and 4.4B, and the ratios (C/N) of the released ion concentrations in the CO₂ case over that of the N₂ with HCl case were calculated. Within 44 h reaction time, the released ion concentrations were similar: the C/N value for K was 1.1 ± 0.1, and the C/N values for Mg, Al, Si, and Fe were 0.9 ± 0.1. Over the 70–144 h reaction period, higher dissolved ion concentrations were observed under the CO₂ case (Figure 4.2A) than the N₂ with HCl case (Figure 4.4B): the C/N ratio for K was 1.2 ± 0.1, and the C/N values for Mg, Al, Si, and Fe were 1.6 ± 0.2. The higher dissolved ion concentrations after reaction for longer times (70–144 h) for the CO₂ case can be caused by the
observed earlier biotite cracking (Figures 4.1A and 4.3B), which resulted in increased surface area in contact with solution, and thus accelerated the ion release greatly.

The temperature, pressure, salinity, and pH (Figure 4-S4) values in these two cases were the same within 44 h, while the dissolved bicarbonate (0.7 mM for the CO₂ case and 0 mM for the N₂ with HCl case, based on GWB calculations) concentrations were different. Thus, the similar released ion concentrations within 44 h indicated that the effect of bicarbonate complexation on ion release from biotite under these conditions is minor. On the other hand, within 44 h reaction time, surface morphological evolutions for the two cases were significantly different: cracking of the biotite basal surface was promoted in the CO₂ case. Considering the similarity of other parameters of the two systems, the promoted cracking in the CO₂ case should be caused by the dissolved CO₂ molecules.

To identify the possible mechanisms for the promoted biotite cracking by the dissolved CO₂ molecules, we first recalled the cause of mica surface cracking: crack formation on mica basal surfaces has been broadly observed after reaction in salt solutions, through swelling of the mica interlayer, caused by cation exchange reactions (i.e., the exchange of bigger hydrated cations in the salt solution with the smaller biotite interlayer K⁺).40, 69, 106 Regarding the mechanisms that promote the mica cracking, in our previous study, we found that the swelling degrees of clay can control the ease of crack formation. For example, hydrated Ca²⁺, which is bigger than the hydrated Na⁺, can cause more significant swelling of the biotite interlayer by ion-exchange with K⁺, resulting in earlier cracking of the biotite basal surface.106

In this study, both CO₂ and N₂ comparison experiments were conducted in 1 M NaCl solutions. Thus, the same cation exchange reactions (Na⁺–K⁺ exchange) occurred in both cases.
To explain the promoted cracking in the CO$_2$ case, we sought factors related to CO$_2$ behavior, other than the identity or size of hydrated cations in brine, which can cause enhanced biotite interlayer swelling.

Fortunately, because of the recent recognition of the importance of CO$_2$–caprock interactions at GCS sites, in most recent years, there has been a surge of studies on the intercalation of CO$_2$ molecules into clay interlayers. Tables 3-S3 summarizes some of these studies. These recent studies used montmorillonite as a representative clay, and its swelling during CO$_2$ exposure has been broadly reported in both experimental observations and molecular simulations.\textsuperscript{111-116} Regarding mica, molecular simulations have shown that CO$_2$ molecules can stably exist in muscovite (white mica) interlayers and that bonds form between CO$_2$ and muscovite.\textsuperscript{66} In addition, in most of the experimental studies, N$_2$ was used as a comparison to CO$_2$, and no significant swelling of the clay was observed from exposure to N$_2$.\textsuperscript{111,112,114,117} To date, however, no molecular mechanisms have been reported to account for the different roles of CO$_2$ and N$_2$ molecules in clay swelling.

Based on the reasoning above, we suggest that the observed promoted biotite surface cracking in the CO$_2$ case could be caused by enhanced biotite swelling, through the intercalation of CO$_2$ molecules into the biotite interlayer. However, there is a caveat to this conclusion. In the reported studies of CO$_2$ intercalation into clay (Table 4-S3), CO$_2$ was in the pure supercritical phase, pure gas phase, or the gas phase with water molecules. To the best of our knowledge, no research has reported the intercalation of CO$_2$ molecules in brine into clay interlayer.

At GCS sites, caprock could interact with both dry to water-saturated scCO$_2$ and CO$_2$ molecules dissolved in brine. However, so far, no $d$-spacing measurements have been conducted
for the potential clay swelling caused by interaction with CO₂ molecules in brine, because of the technical difficulty in conducting *in situ* X-ray diffraction (XRD) measurements for the CO₂–brine–mica system under high CO₂ pressure and high temperature conditions. Here, we made the first nano-scale observation of the promoted mica cracking by CO₂ molecules in brine. Considering the importance of the interaction of clay with CO₂ molecules in brine at GCS sites, our observations provide a good stepping stone for future experimental observations or molecular simulations of the intercalation of CO₂ molecules in brine into clay interlayers.

### 4.3.3 CO₂–Brine–Biotite Interactions at Varied CO₂ Pressures Relevant to GCS

In the above section, by comparing two systems with and without CO₂, we found that CO₂ molecules in brine could promote biotite surface cracking and thus its later dissolution. At GCS sites, CO₂ molecules always exist, while the CO₂ pressure, temperature and brine salt compositions vary greatly, all of which determine the concentrations of dissolved CO₂ molecules in brine. Under higher CO₂ pressure, lower temperature, and lower salinity conditions, there are higher concentrations of dissolved CO₂ molecules in brine.⁷³ Thus, to investigate whether different CO₂ pressures relevant to GCS sites affect the CO₂–brine–biotite interactions, we conducted experiments for 22 h at both low (35 °C) and high (95 °C) temperatures under 75, 102, and 120 atm CO₂. Based on GWB calculations (Table 4.1), at 35 °C over the CO₂ pressure range of 75–120 atm, the CO₂(aq) activity is in the range of 1.52–2.39, and the pH value is in the range of 2.84–2.95. At 95 °C over the CO₂ pressure range of 75–120 atm, the CO₂(aq) activity is in the range of 0.59–0.94, and the pH value is in the range of 3.13–3.23.
Table 4.1 GWB calculated solution initial ionic strengths, pH values, and CO$_2$(aq) and HCO$_3^-$ concentrations and activities under different temperatures and CO$_2$ pressures

<table>
<thead>
<tr>
<th>CO$_2$ pressure (atm)</th>
<th>75</th>
<th>120</th>
<th>102</th>
<th>102</th>
<th>102</th>
<th>102</th>
<th>75</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>55</td>
<td>75</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Ionic strength (M)</td>
<td>1.04</td>
<td>1.06</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>pH</td>
<td>2.95</td>
<td>2.84</td>
<td>2.88</td>
<td>2.97</td>
<td>3.07</td>
<td>3.16</td>
<td>3.23</td>
<td>3.13</td>
</tr>
<tr>
<td>CO$_2$(aq) Concentration (M)</td>
<td>1.19</td>
<td>1.87</td>
<td>1.61</td>
<td>1.11</td>
<td>0.83</td>
<td>0.66</td>
<td>0.49</td>
<td>0.77</td>
</tr>
<tr>
<td>CO$_2$(aq) activity coefficient</td>
<td>1.27</td>
<td>1.28</td>
<td>1.28</td>
<td>1.25</td>
<td>1.23</td>
<td>1.21</td>
<td>1.21</td>
<td>1.21</td>
</tr>
<tr>
<td>CO$_2$(aq) activity</td>
<td>1.52</td>
<td>2.39</td>
<td>2.05</td>
<td>1.39</td>
<td>1.02</td>
<td>0.80</td>
<td>0.59</td>
<td>0.94</td>
</tr>
<tr>
<td>HCO$_3^-$ concentration (mM)</td>
<td>0.86</td>
<td>1.06</td>
<td>0.99</td>
<td>0.89</td>
<td>0.78</td>
<td>0.67</td>
<td>0.58</td>
<td>0.73</td>
</tr>
<tr>
<td>HCO$_3^-$ activity coefficient</td>
<td>0.68</td>
<td>0.68</td>
<td>0.68</td>
<td>0.67</td>
<td>0.67</td>
<td>0.65</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td>HCO$_3^-$ activity (10$^{-3}$)</td>
<td>0.58</td>
<td>0.72</td>
<td>0.67</td>
<td>0.60</td>
<td>0.52</td>
<td>0.44</td>
<td>0.38</td>
<td>0.47</td>
</tr>
</tbody>
</table>

At either 35 or 95 °C, similar released ion concentrations were observed over the pressure range (Figure 4.5). This agreed with our conclusion in Section 3.2 that the direct effects of bicarbonate complexation on ion release from biotite under our conditions were minor.

**Figure 4.5.** Dissolved ion concentrations after reaction of the biotite flakes in 1 M NaCl solution at 95 °C (A) and at 35 °C (B) under 75–102 atm CO$_2$ for 22 h. The concentrations are normalized by the stoichiometry of the biotite formula $\left[ \text{K}_{0.91}\text{Na}_{0.08}(\text{Mg}_{0.52}\text{Mn}_{0.02}\text{Fe}_{0.37}\text{Ti}_{0.04})_3(\text{Al}_{1.00}\text{Si}_{3.00})\text{O}_{10}(\text{F}_{0.43}\text{OH}_{0.57})_2 \right]$ to identify the dissolution congruency. The K concentrations are much higher than the framework ions (Mg, Fe, Al, and Si) and are divided by a factor of 10.
Regarding the effects of CO$_2$ on biotite surface morphological evolutions, at either 35 °C or 95 °C, similar surface morphology was observed on the reacted biotite surfaces over the pressure range: numerous illite fibers precipitated on the surfaces. At 35 °C, no cracking occurred (Figure 4.6). At 95 °C, cracks with similar depth (12 ± 5 nm) were observed by AFM imaging of the surfaces reacted under different CO$_2$ pressures in the range of 75–120 atm.

<table>
<thead>
<tr>
<th></th>
<th>75 atm</th>
<th>102 atm</th>
<th>120 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. 95 °C</strong></td>
<td><img src="A1" alt="Image" /></td>
<td><img src="A2" alt="Image" /></td>
<td><img src="A3" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>cracks</td>
<td>crack</td>
<td>cracks</td>
</tr>
<tr>
<td><strong>B. 35 °C</strong></td>
<td><img src="B1" alt="Image" /></td>
<td><img src="B2" alt="Image" /></td>
<td><img src="B3" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.6.** Height mode AFM images of biotite basal planes after reaction of single biotite flakes in 1 M NaCl under 75–102 atm CO$_2$ at 95 °C (A) and at 35 °C (B) for 22 h. The size of all the images is 50 μm × 50 μm.

For the effects of CO$_2$ pressure on its intercalation into clay, recent studies (Table 4-S3) showed that at relatively high CO$_2$ pressure, a further increase of CO$_2$ pressure did not affect the swelling of the clay; while at low CO$_2$ pressure, increasing the CO$_2$ pressure promoted the swelling of clay layers. Although the threshold of the critical CO$_2$ pressure has not been identified yet, based on Giesting et al.’s research, increasing CO$_2$ pressure from 49 to 632 atm...
did not result in significant further increase of the $d_{001}$ spacing of the clay. At different GCS sites, the CO$_2$ pressures can vary, but they are always higher than the 49 atm reported here. Thus, it is likely that different CO$_2$ pressures at GCS sites may not significantly affect the swelling and cracking of the clay in brine, as reported here.

4.4 Conclusions

In this study, biotite dissolution experiments were conducted at varied temperatures relevant to GCS conditions. With increasing temperature, faster dissolution and earlier swelling-induced biotite surface cracking were observed, and the transition from preferential dissolution of Mg, Fe, and Al over Si to congruent dissolution of biotite framework ions (Mg, Fe, Al, and Si) was also observed. Based on Si release rates, the activation energy of biotite dissolution was calculated to be $52 \pm 5$ kJ mol$^{-1}$, which can be used for geochemical simulations to better predict the fate and transport of CO$_2$ under GCS conditions.

We also differentiated the effects of CO$_2$ on the CO$_2$–brine–biotite interactions. Interestingly, the CO$_2$ injection–induced CO$_2$–brine–biotite interactions were not only caused by the pH decrease of the brine, but also by the molecular behavior of CO$_2$, which can promote cracking of the biotite surface. The cracking caused the detachment and mobilization of fibrous illite, which can cause significant decrease in aquifer permeability. The biotite surface cracking also increased the surface area of biotite in contact with solution, and hence enhanced its later ion release.

Based on the swelling mechanism of crack formation and the broadly reported clay swelling by CO$_2$ molecule intercalation in both the gas and supercritical phases, we suggested that the CO$_2$ molecules in brine could also get into the biotite interlayer, which enhanced the swelling of the biotite interlayer and thus its cracking. This report sheds new light on
intercalation of CO$_2$ into clay layers in the presence of bulk brine. Our observations indicate several Direct experimental observations and molecular simulations of CO$_2$ into clay layers in the presence of bulk brine can be important future directions. Also, for safe GCS operations, it is essential to evaluate the porosity, permeability, and seal integrity changes of the caprock caused by CO$_2$-enhanced clay swelling in the presence of bulk brine.

**Acknowledgments**

This work is supported by the NSF CAREER AWARD (EAR-1057117) and Washington University’s Consortium for Clean Coal Utilization. We would like to acknowledge Jessica R. Ray for HR-TEM measurements and Qingyun Li for experimental help.
Supporting Information for Chapter 4

Contents: Experimental Design Details

Three Tables (4-S1 – 4-S3)

Five figures (4-S1 – 4-S5)

Experimental Design. The pressure and temperature ranges for the four sets of batch experiments were chosen to be relevant at GCS sites. In deep saline aquifers, Na\(^+\) and Cl\(^-\) are the most abundant cation and anion, respectively. In the local brine, which is in, or close to, equilibrium with respect to biotite, there are high concentrations of NaCl as well as the ions dissolved from biotite (including K\(^+\) and the framework ions). However, during CO\(_2\) injection or CO\(_2\) leakage, the local brine is replaced by brine with new compositions, which may not contain dissolved ions from biotite. Considering the varied ion compositions of the replacing brine, and diverse aqueous chemistries of field sites, in this study, we just used 1 M NaCl, which is the major salt in brine, to mimic the brine composition.

For the experiments conducted at both low (35 °C) and high (95 °C) temperatures at 75, 102, and 120 atm of CO\(_2\) pressures, a reaction time of 22 h was chosen because, based on our previous study,\(^{69}\) 22 h was around the initial time point when cracks started to form after reaction at 95 °C. Thus we could observe the effects of different CO\(_2\) pressures on the cracking formation. Also, within this time period, the reacting surface area of the biotite could be better controlled, so we could compare the dissolved ion concentrations.
Figure 4-S1. Experimental setup for the high temperature and high pressure batch experiments.
Figure 4-S2. Experimental setup for the high temperature and high pressure in-situ pH measurements.
Figure 4-S3. Activation energy calculations of biotite dissolution based on Si release rates at different temperatures. Si release rates are normalized according to the stoichiometry of the biotite’s formula.
Figure 4-S4. Solution pH values measured by *in situ* pH probes after reaction for different time spans in 1 M NaCl solutions under 102 atm CO$_2$, and under 102 atm N$_2$ (with the same initial solution pH adjusted by adding HCl).
Figure 4-S5. Height profiles of fibrous illite (A), bump (B), and crack (C) on biotite surfaces after reactions in 1 M NaCl under 102 atm CO$_2$ at 75 ºC for 22, 44, and 70 h, respectively. The height profiles below the AFM images are cut along the dotted lines in the corresponding AFM height mode images. Illite fiber heights did not exhibit trends with temperature, pressure, or reaction time. Based on AFM height analysis of 50 illite fibers, their heights were in the broad range of 10–150 nm. The heights of bumps did not exhibit trends with temperature, pressure, or reaction time, either; Based on the height analysis of 30 bumps, the typical heights of bumps were around 18 ± 6 nm. The depths of cracks were around 10–20 nm under all our experimental conditions (on the basis of AFM height analysis of 50 cracks), except for after reactions in 1 M NaCl under 102 atm CO$_2$ at 95 ºC for 44 h (Figure 4.1A3) and 70 h (Figure 4.1A4). Under these conditions, the crack depths were 31 ± 6 and 57 ± 8 nm (on the basis of AFM height analysis of 20 cracks under each condition), respectively. The size of all the images is 50 μm × 50 μm.
Table 4-S1. The temperature, pressure, and injection depth at different GCS field sites

<table>
<thead>
<tr>
<th>Field Site</th>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>Injection depth (m)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>In Salah field</td>
<td>93</td>
<td>170</td>
<td>1800</td>
<td>92</td>
</tr>
<tr>
<td>Frio-I Brine Pilot test site</td>
<td>59</td>
<td>150</td>
<td>1541–1546</td>
<td>6</td>
</tr>
<tr>
<td>EnCana's CO₂ injection EOR (Enhancing Oil Recovery) project</td>
<td>62</td>
<td>150</td>
<td>1300–1500</td>
<td>7</td>
</tr>
<tr>
<td>Sleipner site</td>
<td>37</td>
<td>100</td>
<td>800–1100</td>
<td>25</td>
</tr>
</tbody>
</table>
Table 4-S2. The d-spacings of illite reference match well with the HR-TEM measured d-spacings of the fibrous precipitates formed after reaction in 1 M NaCl solutions under 102 atm CO$_2$ (A), under 102 atm N$_2$ (B), and under 102 atm N$_2$ with pH adjusted by adding HCl (C).

**A. After reaction in 1 M NaCl under 102 atm CO$_2$**

<table>
<thead>
<tr>
<th>Measured d-spacing (Å)</th>
<th>d-spacing from ref. of illite (Å)</th>
<th>Crystal plane</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.03$^1$</td>
<td>10.02</td>
<td>(0 0 2)</td>
<td>62.3%</td>
</tr>
<tr>
<td>3.86$^2$</td>
<td>3.8915</td>
<td>(1 1 -3)</td>
<td>27.4%</td>
</tr>
<tr>
<td>3.14$^3$</td>
<td>3.1300</td>
<td>(1 1 -5)</td>
<td>31.4%</td>
</tr>
<tr>
<td>2.39$^4$</td>
<td>2.3800</td>
<td>(1 3 3)</td>
<td>29.5%</td>
</tr>
<tr>
<td>2.09$^5$</td>
<td>2.0800</td>
<td>(2 2 3)</td>
<td>10.4%</td>
</tr>
<tr>
<td>1.43$^6$</td>
<td>1.4439</td>
<td>(1 5 7)</td>
<td>1.7%</td>
</tr>
</tbody>
</table>

**B. After reaction in 1 M NaCl under 102 atm N$_2$**

<table>
<thead>
<tr>
<th>Measured d-spacing (Å)</th>
<th>d-spacing from ref. of illite (Å)</th>
<th>Crystal plane</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.48</td>
<td>4.47603</td>
<td>(1 1 -1)</td>
<td>100.0%</td>
</tr>
<tr>
<td>3.58</td>
<td>3.50154</td>
<td>(1 1 -4)</td>
<td>60.5%</td>
</tr>
<tr>
<td>2.64</td>
<td>2.59694</td>
<td>(1 3 -1)</td>
<td>57.3%</td>
</tr>
<tr>
<td>2.28</td>
<td>2.38522</td>
<td>(1 3 3)</td>
<td>29.5%</td>
</tr>
<tr>
<td>1.76</td>
<td>1.75077</td>
<td>(2 2 -8)</td>
<td>3.3%</td>
</tr>
<tr>
<td>1.52</td>
<td>1.52856</td>
<td>(1 3 -11)</td>
<td>13.4%</td>
</tr>
</tbody>
</table>

**C. After reaction in 1 M NaCl under 102 atm N$_2$ with HCl added**

<table>
<thead>
<tr>
<th>Measured d-spacing (Å)</th>
<th>d-spacing from ref. of illite (Å)</th>
<th>Crystal plane</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.48</td>
<td>4.47603</td>
<td>(1 1 -1)</td>
<td>100.0%</td>
</tr>
<tr>
<td>3.58</td>
<td>3.50154</td>
<td>(1 1 -4)</td>
<td>60.5%</td>
</tr>
<tr>
<td>2.57</td>
<td>2.59694</td>
<td>(1 3 -1)</td>
<td>57.3%</td>
</tr>
<tr>
<td>2.28</td>
<td>2.38522</td>
<td>(1 3 3)</td>
<td>29.5%</td>
</tr>
<tr>
<td>1.67</td>
<td>1.75077</td>
<td>(2 2 -8)</td>
<td>3.3%</td>
</tr>
<tr>
<td>1.48</td>
<td>1.52856</td>
<td>(1 3 -11)</td>
<td>13.4%</td>
</tr>
</tbody>
</table>
Table 4-S3 Summary of experimental and simulation studies of clay swelling caused by CO₂

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Results</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental measurements</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca- and Na-montmorillonite, 50°C, 89, 123, and 178 atm, anhydrous N₂ and scCO₂</td>
<td>The amount of swelling or dehydration of clay during exposure to CO₂ depends on the initial H₂O content of the clay. Significant swelling of the clay containing one layer of water hydration was observed with exposure to scCO₂; trivial to no change in the d₀₀₁ spacing was observed when exposed to pressurized N₂, suggesting the swelling was not pressure effect, but was caused by CO₂ intercalation into the clay interlayer. Increasing the scCO₂ pressure from 89 to 123 and 178 atm yielded similar swelling behavior.</td>
<td>111, 112</td>
</tr>
<tr>
<td>Na-montmorillonite, 22–47°C, pressure up to 632 atm, gas and scCO₂</td>
<td>The amount of swelling or dehydration of clay during exposure to CO₂ depends on the initial H₂O content of the clay. Maximum swelling occurred in the sample with the initial d₀₀₁ spacing of 11.3 Å. Little to no expansion occurs for samples with an initial d₀₀₁ spacing of 10.0 Å or in the range of 12.3–12.5 Å. The swelling was confirmed to be not a pressure effect by He gas comparison experiments. Increasing CO₂ pressure from 49 to 632 atms did not result in significant further increase of the d₀₀₁ spacing.</td>
<td>116</td>
</tr>
<tr>
<td>Montmorillonite, -20°C, 5 and 15 atm, N₂ and gas CO₂</td>
<td>Exposure to CO₂ at -20°C, 5 and 15 atm, expansions were observed, with faster expansion occurred at elevated CO₂ pressure of 15 atm. Swelling of the clay was not observed with N₂.</td>
<td>114</td>
</tr>
<tr>
<td>Ca-montmorillonite, 50°C, 89 atm, anhydrous scCO₂</td>
<td>Using a combination of three in situ high-pressure techniques of X-ray diffraction, magic angle spinning nuclear magnetic resonance spectroscopy, and attenuated total reflection infrared spectroscopy, direct evidence was reported for the first time that the expansion of montmorillonite under scCO₂ condition is due to CO₂ migration into the interlayer. Intercalated CO₂ molecules do not appear to react with waters to form bicarbonate or carbonic acid.</td>
<td>113</td>
</tr>
<tr>
<td><strong>Molecular simulations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muscovite, 60°C, 49-296 atm, gas and scCO₂</td>
<td>Molecular dynamic simulations showed that CO₂ molecules can stably exist in muscovite interlayers. There is bond formation between O from CO₂ and H from muscovite’s hydroxyls.</td>
<td>66</td>
</tr>
<tr>
<td>Na-montmorillonite, 45°C, 15 and 99 atm, gas and scCO₂</td>
<td>Using Gibbs ensemble Monte Carlo (GEMC) simulations, the swelling behavior of Na-montmorillonite clay in scCO₂ fluid is thermodynamically favorable. The swelling is inhibited in contact with gas CO₂ at atmospheric pressure. The difference is probably related to different clay adsorption abilities under the two pressures. At high pressure scCO₂, considerable adsorbed CO₂ molecules can result in strong repulsive force, which causes the clay to expand. However, at low pressure, there is only limited adsorption of CO₂ molecules, which cannot produce enough repulsive force within the interlayer region of clay. The interlayer sodium cations are well solvated by surrounding CO₂ molecules.</td>
<td>115</td>
</tr>
</tbody>
</table>

Note: scCO₂: supercritical CO₂
Chapter 5. Environmentally Abundant Anions Influence the Nucleation, Growth, Ostwald Ripening, and Aggregation of Hydrous Fe(III) Oxides

Results of this chapter have been published in Langmuir, 2012, 28 (20), 7737–7746.

Abstract

The simultaneous homogeneous and heterogeneous precipitation of hydrous Fe(III) oxides was investigated in the presence of environmentally ubiquitous anions (nitrate, chloride, and sulfate). Experiments were conducted with $10^{-4}$ M Fe(III) at acidic pH ($\text{pH} = 3.7 \pm 0.2$), which often occurs at acid mine drainage sites or geologic CO$_2$ storage aquifers near injection wells. Quartz was used as a model substrate for heterogeneous precipitation. Small angle X-ray scattering (SAXS) and grazing incidence SAXS (GISAXS), atomic force microscopy (AFM), and dynamic light scattering (DLS) measurements were conducted. In situ SAXS/GISAXS quantified the size, total particle volume, number, and surface area evolutions of the primary nanoparticles formed in the nitrate and chloride systems. In both systems, the heterogeneously precipitated particles were smaller than the homogeneously precipitated particles. Compared with chloride, the volume of heterogeneously precipitated hydrous Fe(III) oxides on the quartz surface was 10 times more in the nitrate system. After initial fast heterogeneous nucleation in both nitrate and chloride systems, nucleation, growth, and aggregation occurred in the nitrate system, whereas Ostwald ripening was the dominant heterogeneous precipitation process in the chloride system. In the sulfate system, fast growth of the heterogeneously precipitated particles
and fast aggregation of the homogeneously precipitated particles led to the formation of particles larger than the detection limit of GISAXS/SAXS. Thus, the sizes of the particles precipitated on quartz surface and in solution were analyzed with AFM and DLS, respectively. This study provides unique qualitative and quantitative information about the location (on quartz surfaces vs. in solutions), size, volume, and number evolutions of the newly formed hydrous iron oxide particles in the presence of quartz substrate and ubiquitous anions, which can help understand the fate and transport of pollutants caused by not only GCS operations, but also in other natural and engineered aqueous environments.

5.1 Introduction

At GCS field sites, the dissolved CO$_2$ lowers the pH of the solution, and thus an increase in Fe concentrations and the release of its adsorbed pollutants were observed near the injection sites. Later on, as the acidic brine flowed and met with the originally neutral brine in the aquifer, the increase in pH caused the precipitation of iron oxides and carbonates, and immobilization of aqueous pollutants. For example, at the Frio-I Pilot GCS site (Gulf Coast, USA), after CO$_2$ injection, there was a sharp increase in dissolved Fe concentration (30-1100 mg/L). There were also increased concentrations of heavy metals, including Zn and Pb, which were originally adsorbed or coprecipitated with iron oxyhydroxides. CO$_2$ injection can also mobilize toxic organics, including toluene and benzene. If large volumes of brine containing mobilized pollutants migrated into potable groundwater (for example, during CO$_2$ leakage), they would have severe environmental impacts. Thus, to study the pollutant transport caused by CO$_2$ injection, the pollutant mobilization and later immobilization associated with the dissolution and re-precipitation of iron oxides were studied at a natural CO$_2$ reservoir at Green River (Utah, USA).
as an analog site for GCS.\textsuperscript{118} Also, reactive transport modeling studies have been conducted.\textsuperscript{6,119} However, the lack of accurate precipitation kinetic data of iron (hydro)oxides, especially for the heterogeneous precipitation process, has significantly hindered the accuracy of reactive transport modeling.

Aside from at GCS sites, hydrous Fe(III) oxide precipitation (i.e., nucleation, growth, Ostwald ripening, and aggregation) plays an important role in many other aquatic systems, where it influences the fate and transport of trace metals and organic pollutants through adsorption, coprecipitation, and redox processes.\textsuperscript{120,121} It can also affect the porosity and permeability of the aquifers based on their location.\textsuperscript{122} Different anions have been reported to affect the precipitation rate\textsuperscript{123-127} of hydrous Fe(III) oxides, as well as the size,\textsuperscript{128,129} charge,\textsuperscript{130} morphology,\textsuperscript{130} composition,\textsuperscript{130} and mineral phase\textsuperscript{123-127} of the particles. These previous studies provide good information about anion effects on hydrous Fe(III) oxide precipitation; however, because of the technical difficulty in quantitatively characterizing the heterogeneously precipitated particles, especially in the early stage of the precipitation process, most previous studies\textsuperscript{123-130} were conducted in the absence of mineral surfaces, and only homogeneous precipitation was characterized.

Water–rock interfaces are ubiquitous on the earth’s surface, and hydrous Fe(III) oxides precipitate simultaneously at these interfaces and in solution. The nucleation, growth, Ostwald ripening, and aggregation rates in the early stage of homogeneous and heterogeneous precipitation determine the location (in solution vs. on mineral surfaces), size, volume, and surface area of hydrous Fe(III) oxide particles. Also, heterogeneous nucleation is an important process which modifies the reactive surface area by forming surface coatings of the particles.\textsuperscript{131} For example, research has shown that quartz coated with iron oxides have much higher reactive
surface area and adsorption capability for heavy metals than pure quartz. However, currently, a shortage of experimental data on the early stage heterogeneous precipitation significantly hinders more accurate reactive transport modeling. Thus, to better predict the fate and transport of pollutants in the environment, it is important to characterize the early stage simultaneous precipitation in the presence of mineral surfaces.

In a previous study, we conducted hydrous Fe(III) oxide precipitation experiments in 10 mM NaNO₃ solution with 10⁻⁴ M Fe³⁺ at pH 3.6. Using small angle X-ray scattering (SAXS) and grazing incidence SAXS (GISAXS), we simultaneously quantified the homogeneously and heterogeneously precipitated particles on the quartz surface for the first time. Nitrate ion (NO₃⁻) is abundant at nuclear waste disposal sites. In many other surface and subsurface aquatic systems, such as geologic CO₂ sequestration and acid mine drainage, chloride (Cl⁻) and sulfate (SO₄²⁻) are the most abundant anions. They can behave differently from the nitrate ion, and affect the hydrous Fe(III) oxide precipitation through complexation and adsorption. Therefore, the early stage homogeneous and heterogeneous precipitation of hydrous Fe(III) oxides in the chloride and sulfate systems could be quite different from that in the nitrate system.

The two main foci of the current study were: first, to measure the charge, location, size, volume, number, and surface area evolutions of the particles formed during the early stage of homogeneous and heterogeneous precipitation of hydrous Fe(III) oxides in the presence of environmentally abundant anions (chloride and sulfate), comparison with nitrate was also made; second, to identify the dominant processes (nucleation, growth, Ostwald ripening, and aggregation) happening in these systems. This information can help to determine the fate and transport of pollutants, local porosity and permeability changes, and mineral surface reactivity changes caused by surface coating with hydrous Fe(III) oxides.


5. 2. Experimental Section

5.2.1 Substrate and Solution Preparation

Quartz was chosen as the substrate in this study because it is second only to feldspars as the most abundant mineral in Earth’s continental crust.\textsuperscript{135} Also, artificially grown highly perfect and atomic flat quartz is readily obtainable, while many well ordered natural mineral surfaces and their synthetic analogues are generally difficult to find. Quartz samples (Princeton Scientific Co.) with atomically flat (102) surfaces (Figure 5.1A) were cut into 1 cm × 1 cm squares to fit into the GISAXS/SAXS and DLS cells. The cleaning procedure for the quartz is described in the Supporting Information.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{AFM_images.png}
\caption{Ex situ AFM observations of particles formed on quartz surfaces. Affected by the size of the tip radius, the typical lateral resolution of the tapping mode we used was \(~\)40 nm, which is much bigger than the real particle sizes, and the vertical resolution was sub angstrom. Thus, the real particle sizes were measured accurately in the vertical direction, which are quantified by the line cut curves below the images. In image B, the abundance of aggregates generates a rougher surface.}
\end{figure}

The solutions (Table 5.1) were prepared with reagent grade Fe(NO$_3$)$_3$•9H$_2$O, NaNO$_3$, NaCl, and Na$_2$SO$_4$, and ultrapure water. Sodium was chosen because it is the most abundant cation in
many aquatic systems.\textsuperscript{8, 21} Calculated with Geochemist’s Workbench (GWB, Release 8.0, RockWare, Inc.), the initial ionic strength, pH values, and saturation indices with regard to Fe(OH)_3 were similar in all these solutions (Table 5.1).

**Table 5.1** Initial solution compositions for hydrous Fe(III) oxide precipitation experiments.

<table>
<thead>
<tr>
<th>No.</th>
<th>Fe(NO\textsubscript{3})\textsubscript{3} (mM)</th>
<th>NaCl (mM)</th>
<th>NaNO\textsubscript{3} (mM)</th>
<th>Na\textsubscript{2}SO\textsubscript{4} (mM)</th>
<th>IS\textsuperscript{a} (mM)</th>
<th>pH\textsubscript{initial}\textsuperscript{b}</th>
<th>SI\textsuperscript{c} _Fe(OH)_3</th>
<th>(\zeta\textsuperscript{d} ) (mV)</th>
<th>(\zeta\textsuperscript{e} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>10</td>
<td>3.7 ± 0.1</td>
<td>0.31</td>
<td>35.1 ± 4.0</td>
<td>60.6 ± 5.7</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>3.7 ± 0.1</td>
<td>0.31</td>
<td>38.1 ± 4.8</td>
<td>52.8 ± 7.8</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>3.42</td>
<td>10</td>
<td>3.8 ± 0.1</td>
<td>0.41</td>
<td>2.1 ± 5.8</td>
<td>0.3 ± 0.6</td>
</tr>
</tbody>
</table>

Note: \textsuperscript{a}IS: Ionic Strength. \textsuperscript{b}pH values were measured right after mixing, and are consistent with GWB calculations. \textsuperscript{c}SI (=\text{log}(Q/K)): Saturation Index with respect to Fe(OH)_3. Fe(OH)_3 was used to represent ferrihydrite for simplicity. Log K = -7.22 at 20\textdegree C was calculated using the thermo.dat GWB database file.

\textsuperscript{d}The zeta potential (\(\zeta\)) values were measured without quartz powder every 1 min for 1 hr. During the first 20 minutes, the signals were too weak and the values were unstable because very few precipitates had formed. Between 20 minutes and 1 hr, the values were stable and are given here.

\textsuperscript{e}The zeta potential (\(\zeta^*\)) values were measured with quartz powder every 1 min for 1 hr. The values were stable throughout the 1 hr experiments. The presence of quartz powder in solution provides the surface for Fe(III) oxide precipitation. Thus, compared with the experiments conducted without quartz powder, stronger scattering signal was generated at the beginning, and more stable zeta potential values were reported. The differences in the zeta potential values measured with and without quartz powder may be related to the different signal/noise ratios of the data obtained. Nevertheless, with the two methods, the trend of the zeta potentials among different anions is consistent; thus, it is useful for interpretation of the mechanisms related to electrostatic forces.

### 5.2.2 In Situ SAXS/GISAXS Measurements

For each *in situ* run, a fresh quartz substrate was placed inside a specially designed SAXS/GISAXS fluid cell,\textsuperscript{42} and the top surface of the substrate was aligned with the middle of
the X-ray beam, which was focused vertically to deliver a beam height of 100 μm. As soon as 1 ml of freshly mixed solution (Table 5.1) was injected into the SAXS/GISAXS cell, *in situ* SAXS/GISAXS measurement started. During the measurement, the cell was moved alternately up and down by 1 mm at 1 min intervals. Therefore, time-resolved scattering signals were collected from particles on the substrate (via GISAXS) and in solution (via SAXS). The geometry of the SAXS/GISAXS measurements and more details can be found in Figure 5-S1. Experiments were conducted at beamline 12 ID-B at the Advanced Photon Source (APS), Argonne National Lab (ANL), IL.

5.2.3 Analysis of SAXS/GISAXS Scattering Data and Calculation of Total Volume, Size, Number, and Surface Area of the Primary Particles

First, the background signal, the 2D scattering image from pure water, was subtracted from each 2D image. Then, the subtracted 2D images were reduced to 1-D. For each SAXS image, the intensities were azimuthally averaged over the 2D image at each scattering vector (q, unit: Å⁻¹). For GISAXS, line-cuts were made along the Yoneda wing, where the scattering signal is enhanced along the in-plane direction due to the grazing incidence effect in GISAXS.¹³⁶,¹³⁷ The 1-D GISAXS and SAXS intensities (I) plotted over q are shown in Figures 5.2A and 5.2B, respectively. In this study, the q range measured for GISAXS/SAXS was around 0.005 – 0.250 Å⁻¹. Because q is reciprocally related to the radius of the particle (R) with the approximation (R = π/q), the measurement range for particle size was approximately 1– 63 nm. In order to compare GISAXS with SAXS intensities quantitatively, the intensities were further normalized by the enhancement factor at the Yoneda wing and by the ratio of the effective X-ray beam sizes hitting the substrate and the solution. GISAXS data reduction was performed with the GISAXS-SHOP
macro, available at the APS beamline 12 ID. The data reduction procedure is detailed in the Supporting Information of our previous paper.\textsuperscript{42}

The invariant $Q$, which is defined as $Q = \int_{0}^{\infty} I(q)q^2 dq$, is proportional to the total volume of nanoparticles.\textsuperscript{138} Based on this definition, Lorentz-corrected\textsuperscript{138} GISAXS and SAXS intensities (i.e., $I \times q^2$) are plotted over $q$ in Figures 5.3A1-A3 and 5.3B1-B3, respectively. The integrated areas under the Lorentz-corrected plots ($= Q$) provide relative total particle volumes (Figure 5.4A). To get the evolution of the average primary particle sizes, the 1D scattering curves (Figure 5.2A) were fit to a polydisperse sphere model with the Schultz distribution as a size distribution function, and structure factors were also included to model the interactions of these primary particles. More details are provided in the Supporting Information.\textsuperscript{139} Then, using the total particle volumes (Figure 5.4A) and the average primary particle sizes (Figure 5.4B), the total particle numbers (Figure 5.4C) and surface areas (Figure 5.4D) of primary particles were calculated. All data analysis was performed with the Igor Pro program (V. 6.22A, WaveMetrics, Inc., Oregon).

5.2.4 Zeta Potential ($\zeta$), Hydrodynamic Particle Size, and Atomic Force Microscopy (AFM) Measurements

A Zetasizer instrument (Nano ZS, Malvern Instruments Ltd.) was used for zeta potential and hydrodynamic particle size measurements. Each freshly mixed solution (Table 5.1) was injected into a zeta cell (DTS1060C, Malvern Instruments), with and without quartz powder in solution, and zeta potential measurements were performed every 1 min for 1 h at 20 °C. Because of the technical limitations in measuring the zeta potential of the (102) surface of single quartz crystals, we measured the zeta potential of quartz powders suspended in each acidic salt solution.
(NaNO₃, NaCl, or Na₂SO₄, all with an ionic strength of 10 mM and pH around 3.7 ± 0.2). To measure the hydrodynamic sizes of the homogeneously precipitated particles, a fresh 1 cm × 1 cm quartz sample was placed in a dynamic light scattering (DLS) cell (DTS0012, Malvern Instruments Ltd.), and 1 ml of freshly mixed solution (Table 5.1) was injected into the cell. The hydrodynamic sizes of the homogeneously precipitated particles in solution were measured every 1 min for 1 h at 20 °C, as a supplement to the SAXS measurements.

At the end of each GISAXS/SAXS experiment, *ex situ* AFM measurements were conducted to observe both nano- and micro-scale particles on the quartz surface, as a complement to the *in situ* GISAXS measurements. AFM tapping mode (AFM, Veeco Inc.) was used. Height, amplitude, and phase images were collected simultaneously. Probes were 125 μm long, with phosphorus (n) doped silicon tips (a nominal tip radius of 10 nm, MPP-11100-10, Veecoprob). The drive frequencies were between 312-320 kHz, typical spring constants were 20-80 N/m, and scan rate was 0.80 Hz. Nanoscope 7.20 software was used to analyze topographic features.

### 5.2.5 Precipitate Phase Identification

To identify the phase of particles precipitated on the quartz surface, we conducted *ex situ* GIWAXS for the particles precipitated on quartz that had undergone SAXS/GISAXS runs within 24 hrs. Even for the *ex situ* GIWAXS measurements, which can generate much stronger signals than *in situ* GIWAXS measurements, no diffraction pattern was observable. Hence, the particles on the quartz surface were either amorphous or their amounts were too small to be detected.

To identify the particles formed in solution, *in situ* wide angle X-ray scattering (WAXS) measurements were conducted simultaneously during SAXS/GISAXS experiments: no diffraction pattern was observable. Thus, the particles were also either amorphous or their amounts were under the detection limit. For *ex situ* phase identification of the particles formed in
solution, we used synchrotron-based high resolution X-ray diffraction (HRXRD) analysis, which requires only small sample volumes. The particles in solution were collected by centrifuge, stored in Kapton® capillary tubes at room conditions, and sent to sector 11-BM of the APS at ANL, where HRXRD analysis was performed within 7 days after sample preparation. Details of the sample preparation are provided in the Supporting Information.

5.3. Results and Discussion

5.3.1 Sizes of the Particles Precipitated on the Quartz Surface and in Solution

Figures 5.2A1-A3 show the GISAXS scattering intensities from particles on the quartz surface. The shapes of the GISAXS scattering curves in the presence of nitrate and chloride are different in the low $q$ range (Figures 5.2A1 and 5.2A2). In the nitrate system (Figure 5.2A1), as $q$ gets close to 0, the intensity increases, indicating the aggregation of primary particles. This finding was confirmed by AFM observations: in the presence of nitrate, primary particles as well as many aggregates were observed on the quartz surface (Figure 5.1B); while in the chloride system, only primary particles were observed (Figure 5.1C).
A1-A3: Scattering intensity from particles on the quartz surface

B1-B3: Scattering intensity from particles in solution

Figure 5.2. GISAXS scattering intensities cutting around the Yoneda wing from particles on quartz surfaces immersed in 10^{-4} M Fe^{3+} solutions with 10 mM NaNO_3 (A1), 10 mM NaCl (A2), or 3.42 mM Na_2SO_4 (A3). The black lines show the fitted curves. The GISAXS/SAXS experiments were conducted for 2 hr in the case of nitrate and chloride. In the case of sulfate, because of formation of big particles out of the GISAXS/SAXS measurement range, experiments were run for only 1 hr. SAXS scattering intensities from particles precipitated in the solutions were averaged over the 2D detector at each q value (B1-B3). The in situ GISAXS/SAXS experiments were conducted at 20 °C. Throughout the experiments, water evaporation was very slow and no significant volume change of the original 1 ml solution occurred.

Lorentz-corrected GISAXS intensities are shown in Figures 5.3A1-A3. In both nitrate and chloride systems, the Lorentz-corrected GISAXS intensity curves show a triangular shape over the q range measured (Figures 5.3A1, 5.3A2), and the corrected intensities are close to zero at
both the upper and lower bounds of the measured $q$ range. The shape and intensity values indicate that the sizes of the primary particles on the quartz surfaces were within the $q$ range measured. This indication was further confirmed by AFM observations: after reactions in both nitrate (Figure 5.1B) and chloride (Figure 5.1C) systems, primary particles smaller than 10 nm were observed on the quartz surfaces. As the reactions went on, shifts of the peak positions to the lower $q$ range were observed (marked by the arrows in Figures 5.3A1 and 5.3A2), indicating an increase in primary particle sizes in both systems. To get more accurate in situ particle size information, the scattering curves (Figures 5.2A1 and 5.2A2) were fitted with the polydisperse sphere model with structure factor function included, and the radii of gyration ($R_g$) of the primary particles were calculated (Figure 5.4B). Within 2 hrs, in both nitrate and chloride systems, the radii of the primary particles on the quartz surfaces grew from around 2 to 6 nm (Figure 5.4B). On these quartz surfaces, ex situ AFM measurements conducted in dry condition showed 2–4 nm primary particles (Figures 5.1B and 5.1C), which were slightly smaller than the sizes measured by in situ GISAXS at the end of the 2 hr experiments (~ 6 nm). This difference could be due to the dehydration of the ex situ samples. In the presence of nitrate, after reaction for 40 min, a new additional peak shows up on the Lorentz-corrected GISAXS curve (Figure 5.3A). The formation of the new peak in the high $q$ region (indicated by the bar in Figure 5.3A) indicated that besides the growth of the particles formed earlier, small new nuclei formed. The radius of gyration ($R_g$) of the newly formed nuclei was calculated to be 1 nm.
A1-A3: Lorentz-corrected scattering intensity from particles on the quartz surface

B1-B3: Lorentz-corrected scattering intensity from particles in solution

Figure 5.3. Lorentz-corrected GISAXS/SAXS intensity curves from particles on the quartz surfaces and in solutions. The dashed lines in images B1 and B2 are used for the extrapolation of the invariant calculations, as described in the Supporting Information.

For the particles formed in solution, the Lorentz-corrected SAXS intensities are shown in Figures 5.3B1-B3. For both the nitrate and chloride systems, as the reactions proceed, the Lorentz-corrected SAXS intensity curves (Figures 5.3B1 and 5.3B2) show shifts to an even lower $q$ range (marked by the arrows) than the GISAXS curves (Figures 5.3A1 and 5.3A2), indicating a faster increase of primary particle sizes in these solutions than on the quartz surfaces. Because the SAXS intensities were weaker and noisier than the GISAXS intensities, the radii of the particles in these solutions were estimated using the approximation ($R_g = \pi/q$), where the $q$ values at the peak positions (indicated by arrows in Figures 5.3B1 and 5.3B2) of the Lorentz-
corrected intensity curves were chosen. The calculated radii are shown in Figure 5.4B. Within 2 hrs, the particles in solution grew from 3.3 ± 1.7 to 20.9 ± 7.4 nm in the nitrate system, and they grew from 3.1 ± 1.4 nm to 27.4 ± 3.7 nm in the chloride system. Considering the uncertainty of the estimated particle sizes, at the end of the 2 hr experiments, the difference between the particle sizes formed in the nitrate and chloride solutions were within the error range, and the particles precipitated in these two solutions were significantly larger than those precipitated on these quartz surfaces.

To complement SAXS observations, the hydrodynamic size evolutions of the particles in solution were measured by DLS. For Rayleigh light scattering, the scattering intensity is proportional to the 6th order of the particle size.\(^{140}\) Therefore, in both nitrate and chloride systems, the light scattering intensities generated by the small amount of small nanoparticles were too low to give reliable hydrodynamic particle size information.

For the sulfate case, the shapes of the Lorentz-corrected GISAXS (Figure 5.3A3) and SAXS (Figure 5.3B3) curves are not triangular. Instead, as \(q\) decreases, continuous increases in the corrected intensity are observed, indicating the formation of large primary particles out of the GISAXS/SAXS measurable range. Thus, it is improper to use GISAXS/SAXS data to calculate the in situ sizes of the big primary particles. On the other hand, the large particles precipitated in the sulfate solution generated sufficiently strong signals for successful DLS measurements to determine their hydrodynamic particle sizes. Within 1 h, the hydrodynamic particle sizes of the particles formed in solution increased from 243 ± 43 to 1868 ± 57 nm (diamond symbols in Figure 5.4B), bigger than the primary particles (2 – 100 nm) on the quartz surface at the end of the 1 hr experiment observed by ex situ AFM (Figure 5.1D and 5.1E). A very small amount of micro-sized aggregates (Figure 5-S2) was also observed on the quartz surface after reaction.
5.3.2 Volumes of the Particles Precipitated on the Quartz Surface and in Solution

As discussed in Section 3.1, the big particles formed in the presence of sulfate were out of the measurement range of GISAXS/SAXS; thus, we could not calculate the invariants. In the presence of nitrate and chloride, the calculated invariants, which represent the total particle volumes detected by X-ray in relative units, are shown in Figure 5.4A. The GISAXS invariants calculated between triplicate runs were highly consistent, as indicated by the small error bar in Figure 5.4A. The evolutions of the SAXS invariants fluctuated within the range indicated by the shaded box in Figure 5.4A. Throughout the 2 hr experiments, in nitrate and chloride systems, for the heterogeneously and homogeneously precipitated nanoparticles detected by X-ray, the ratios of the total particle volumes were around 42.6 ± 16.5 and 6.5 ± 2.0, respectively.

A comparison was also made between the nitrate and chloride systems. Interestingly, for the particles on the quartz surface, their total volume in the nitrate system was 10 times greater than those precipitated in the chloride system (Figure 5.4A). To figure out the inhibition mechanisms of chloride on the heterogeneous precipitation of hydrous iron oxide on the quartz surface, two-step reasoning was used: First, we considered the general mechanisms that could inhibit both homogeneous and heterogeneous hydrous Fe(III) oxide precipitation. Second, the specific mechanisms by which chloride could further inhibit heterogeneous precipitation over homogeneous precipitation were considered. The two-step reasoning is explained in detail in the following paragraphs of this section.
Figure 5.4. Evolutions of the total volume (A), average radius (B), total number (C) and surface area (D) of the primary particles precipitated on the quartz surfaces and in the solutions from $10^{-4}$ M Fe$^{3+}$ solutions with 10 mM NaNO$_3$ or NaCl. In image B, the evolution of the hydrodynamic particle sizes of the precipitates formed in $10^{-4}$ M Fe$^{3+}$ and 3.42 mM Na$_2$SO$_4$ solution are read from the right Y-axis.

Regarding the general mechanisms that could inhibit both homogeneous and heterogeneous hydrous Fe(III) oxide precipitation, we considered the steps included during hydrous Fe(III) oxide precipitation: First, hydrolysis of the ferric iron forms the monomer (eqn. (1)). Then, dimers and polymers can form through continuous olation (hydroxo–bridging) and oxolation (oxo–bridging) reactions (eqn. (2) and (3)).

Once the polymer size is larger than the critical nucleus size, stable nuclei form, and hydrous Fe(III) oxide precipitation occurs.
\textbf{Hydrolysis}: \[ \text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3 \text{H}^+ \] (1)

\textbf{Olation}: \[ 2[\text{Fe(H}_2\text{O)}_5\text{OH}^{2+}] \rightarrow [(\text{H}_2\text{O})_4\text{Fe-(OH)}_2-\text{Fe(H}_2\text{O})_4]^{4+} + 2\text{H}_2\text{O} \] (2)

\textbf{Oxolation}: \[ 2[\text{Fe(H}_2\text{O)}_5\text{OH}^{2+}] \rightarrow [(\text{H}_2\text{O})_4\text{Fe-O-Fe(H}_2\text{O})_5]^{4+} + \text{H}_2\text{O} \] (3)

Considering the precipitation process, several possible mechanisms may be responsible for slowing ferric ion precipitation in the presence of chloride: First, different mineral phases may form in the presence of nitrate and chloride, and the phase formed in the presence of chloride might be more soluble. Thus, the solution would be less saturated with respect to the potential secondary mineral phase, resulting in slower precipitation kinetics. However, HRXRD measurements showed that ferrihydrite formed in both solutions (Figure 5-S3 in Supporting Information), which ruled out this possibility. There is a caveat that these \textit{ex situ} samples might change during the 7-day aging before we performed HRXRD measurements. Also, because of the technical difficulties in identifying the particles on quartz surfaces (discussed in Section 2.5), we measured only the particles formed in the solutions.

A second possible mechanism slowing the precipitation is that the chloride ions might inhibit the hydrolysis of the ferric ions in solution (eqn. (1)). If so, the pH decrease of the ferric solution would be slower in the presence of chloride, because the hydrolysis reaction releases protons into the solution (eqn. (1)). However, pH measurements of the two solutions showed the same trend (Figure 5-S4 in Supporting Information); thus, this possibility is also ruled out.

A third possibility is that chloride ions might form relatively strong inner-shell complexes, as shown by X-ray adsorption spectrometry (XAS), which can slow the olation and oxolation reactions.\textsuperscript{128} Compared with chloride, nitrate ions are not so tightly bound to ferric ions, and they can be exchanged for OH\textsuperscript{−} or O\textsuperscript{2−} ligands.\textsuperscript{128}
To sum up, by ruling out the first two mechanisms, we concluded that in our system, the most likely general mechanism for the chloride inhibition of both homogeneous and heterogeneous hydrous Fe(III) oxide precipitation is the formation of inner-shell complexes of chloride with the ferric ion, which hinders the polymerization and thus the following precipitation process.

If this general inhibition mechanism is the only role that chloride played in the system, then, chloride should have inhibited both the homogeneous and heterogeneous precipitation to the same extent. However, considering the uncertainty of the SAXS invariants (the box in Figure 5.4A), the SAXS invariants in nitrate and chloride systems should not vary by more than 5 times. For the GISAXS invariants, at the end of the 2 hr experiments, in the nitrate system, the total particle volume on the quartz surface was 10 times more than that formed in the chloride system.

Thus, considering the enhanced difference between the nitrate and chloride systems in heterogeneous precipitation on the quartz surface compared to the homogeneous precipitation, more specific mechanisms by which chloride might further inhibit the heterogeneous precipitation were considered: First, higher local Cl\textsuperscript{−} concentrations at the interface than in the bulk solution have been reported by both simulations\textsuperscript{143} and experiments.\textsuperscript{144,145} The viscosity of a 7 mM aqueous NaCl solution obtained at a surface separation < 1 nm was 2–4 orders of magnitude larger than the bulk value.\textsuperscript{145} In addition, as revealed by X-ray CTR scattering measurements and MD simulations, the local Cl\textsuperscript{−} concentration close to a negatively charged mica surface has been reported to be around one order of magnitude higher than that in the bulk.\textsuperscript{146} In our system, the local Cl\textsuperscript{−} concentrations near the quartz surface could be much higher than those in the bulk solution, causing more significant inhibition of the precipitation on the quartz surface than in solution.
Second, the electrostatic attractive force between the iron oxides and the quartz surface may be weaker in the presence of chloride than in the presence of nitrate, which could slow the precipitation at the quartz surface. However, the zeta potential of the iron oxides precipitated in the chloride system ($\zeta = 52.8 \pm 7.8$ and $38.1 \pm 4.8$ mV, measured with and without quartz powder, respectively, Table 5.1) was similar to that formed in the nitrate system ($\zeta = 60.6 \pm 5.7$ and $35.1 \pm 4.0$ mV, measured with and without quartz powder, respectively, Table 5.1). Also, the zeta potential of quartz in chloride system ($\zeta = -13.8 \pm 1.6$ mV) was similar to that in the nitrate system ($\zeta = -14.3 \pm 2.6$ mV). Thus, similar electrostatic attractive forces between the iron oxides and the quartz surfaces could be expected in the nitrate and chloride systems, and this possibility may be ruled out. However, there is a caveat that the zeta potentials measured with quartz powder might be different from those of single crystal surfaces.

Third, Fourier transform infrared (FTIR) spectroscopy,\textsuperscript{132, 147} Raman spectrometry,\textsuperscript{148} and X-ray photoelectron spectroscopy (XPS)\textsuperscript{147} studies have suggested the formation of Fe–O–Si bonds between coated iron oxides and silica sand.\textsuperscript{147} In the presence of nitrate, the formation of Fe–O–Si could possibly attract ferric ions from the solution to the quartz surface, thus enhancing heterogeneous precipitation on the quartz surface over that in solution (Figure 5.5A). However, in the presence of chloride ions, the ferric ions in solution formed strong inner-shell complexes with the chloride ions.\textsuperscript{128} Thus, the ferric ions could not form the Fe–O–Si bonds with the quartz surface (Figure 5.5B-I), or, Fe–O–Si may form at the quartz surface; however, the complexation of chloride ion with ferric ion can terminate the further polymerization and precipitation at the surface (Figure 5.5B-II). In either way, the enhanced heterogeneous precipitation, which might have occurred in the nitrate system by the formation of Fe-O-Si bonds, could not occur in the chloride system, which also resulted in fewer heterogeneously precipitated particles formed in
the chloride system. Direct experimental observations of the molecular structures of the newly formed nanoparticles at the quartz surface in nitrate and chloride solutions can be an important future research direction, and are beyond the scope of this manuscript.

Figure 5.5. Schematic plot of the potential mechanisms of the enhanced heterogeneous precipitation in the nitrate system (A), and the less heterogeneous precipitation of hydrous Fe(III) oxides on the quartz surface in the chloride system (B). (A) In the nitrate system, the heterogeneous precipitation is enhanced at the quartz surface because the formation of Fe-O-Si bonds could potentially attract the ferric ions to the surface. (B) In the chloride system, two potential cases may happen: (Case I) the Fe-O-Si bond may not be able to form because the ferric ions forms complexes with chloride; or (Case II) the Fe-O-Si bond could form, but further polymerization is inhibited or terminated because the ferric ions form complexes with chloride ions. For simplicity, this diagram does not reflect the exact molecular structures such as bond lengths and angles.

Based on the reasoning above, we concluded that two mechanisms may have been responsible for the enhanced difference between the nitrate and chloride systems in
heterogeneous precipitation on the quartz surface compared to the homogeneous precipitation. First, chloride could inhibit both homogeneous and heterogeneous hydrous Fe(III) oxide precipitation through the formation of strong inner-shell complexes of chloride with the ferric ion, hindering the polymerization. The locally higher Cl\textsuperscript− concentration near the quartz surface than in the bulk solution could enhance the inhibition effect for heterogeneous precipitation over homogeneous precipitation. Second, in the nitrate system, the formation of Fe–O–Si bonds with the quartz surface could promote the heterogeneous precipitation of hydrous Fe(III) oxides. However, in the chloride system, such promoted heterogeneous precipitation could not occur because of the complexation of chloride with ferric ion, also resulting in less heterogeneous precipitation of Fe(III) oxides on the quartz surface than in the nitrate system.

5.3.3 Nucleation, Growth, Ostwald Ripening, and Aggregation

Processes during Hydrous Fe(III) Oxide Precipitation

Different processes can happen during hydrous Fe(III) oxide precipitation, and the number and size of primary nanoparticles may vary accordingly. In our definition (Table 5.2), nucleation, which creates new stable nuclei from solution, increases the primary particle number and maintains the primary particle size. On the other hand, during the growth process, monomers, dimers, and polymers of iron oxides in solution attach to the existing particles. Thus, the primary particle size increases, and the primary particle number remains unchanged. If Ostwald ripening occurs, big particles grow at the expense of the dissolution of small particles; thus, the primary particle size will increase while the primary particle number decreases. During aggregation, two or more primary particles attach together upon collision and form an aggregate, while the shape and size of the primary particles remain unchanged. Thus, the number and the size of primary particles remained the same, while the size of the aggregates increases.
Table 5.2 Changes of primary particle size, total number and volume during different precipitation processes.

<table>
<thead>
<tr>
<th></th>
<th>Nucleation</th>
<th>Growth</th>
<th>Ostwald ripening</th>
<th>Aggregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary particle size</td>
<td>=</td>
<td>↑</td>
<td>↑</td>
<td>=</td>
</tr>
<tr>
<td>Primary particle number</td>
<td>↑</td>
<td>=</td>
<td>↓</td>
<td>=</td>
</tr>
<tr>
<td>Total particle volume</td>
<td>↑</td>
<td>↑</td>
<td>=</td>
<td>=</td>
</tr>
</tbody>
</table>

On substrates, in both the nitrate and chloride systems, the primary particle number (Figure 5.4C) increased fast in the early stage of the experiments, indicating a nucleation dominant process. In the nitrate system, during the later stage, both continuous growth of existing particles and nucleation of new 1 nm particles were observed from the Lorentz-corrected GISAXS curve (Figure 5.3A1). Thus, the size of the preexisting primary particles kept increasing, as did the total volume and number of primary particles (Figure 5.4). Aggregation of primary particles was also observed from the GISAXS curve (Figure 5.2A1) and AFM image (Figure 5.1B). On the other hand, in the presence of chloride, in the later stage, the primary particle number decreased, while the primary particle size increased (Figure 5.4), showing an Ostwald ripening dominant process. This is consistent with the GISAXS (Figure 5.2A2) and Lorentz-corrected GISAXS intensity curves (Figure 5.3A2): in the later stage of the chloride system, as the reaction went on, the intensities decreased in the high q region (unit: Å⁻¹, reciprocally related to the particle size) and increased in the low q region, showing that big particles grew at the expense of small particles. In addition, in the chloride system, the area under the Lorentz-corrected GISAXS curve (Figure 5.3A2), which represents the total particle volume (Figure 5.4A), decreased slowly and
continuously after reaction for around 60 min. Initially formed small particles can be highly hydrous, and when these small particles dissolved and big particles grew, less water could be incorporated into the structure of the big particles. Thus, a small and gradual decrease in the total particle volume was observed.

To sum up, for heterogeneous hydrous Fe(III) oxide precipitation on the quartz surface, after the early nucleation dominant period in both nitrate and chloride systems, continuous nucleation, growth, and aggregation occurred in the nitrate system, while Ostwald ripening dominated in the chloride system. To the best of our knowledge, this is the first time that the different dominant processes occurring in the presence of different anions at the early stage of hydrous Fe(III) oxide heterogeneous precipitation were reported. The molecular level mechanisms of how nitrate and chloride influence the different dominant precipitation processes among nucleation, growth, Ostwald ripening, and aggregation requires further study.

Among nucleation, growth, Ostwald ripening, and aggregation, nucleation is the only process which increases the primary particle number. In both nitrate and chloride systems, compared with the particles precipitated on the substrate surfaces, in these solutions, much faster increases of primary particle sizes and much slower increases of total particle volumes were observed throughout the experiments (Figure 5.4). The primary particle number is proportional to the total particle volume and reciprocal to the 3rd order of the primary particle size. Thus, for the particles in solution, the small change of total particle volume and the fast increase in primary particle size indicated a fast decrease in total primary particle number (Figure 5.4C). This means that as reactions went on, new nuclei seldom formed in these solutions, and other processes, which do not increase the primary particle number, were by far more dominant than nucleation.
Potential explanations can be made for the preferred heterogeneous nucleation on the quartz surface rather than in solution: First, heterogeneous nucleation requires less energy than homogeneous nucleation. Second, in our experimental condition (pH = 3.7 ± 0.2), in the presence of nitrate and chloride, the quartz surfaces were negatively charged, with zeta potentials (ζ) of -14.3 ± 2.6 and -13.8 ± 1.6 mV, respectively. Meanwhile, the iron oxide surfaces were positively charged (ζ equals 35.1 ± 4.0 and 38.1 ± 4.8 mV, respectively, Table 5.1). If we assume the iron oxide clusters were also positively charged like the iron oxide nanoparticles, electrostatic attractive forces could attract the iron oxide clusters to accumulate at the quartz surface, making the local solution near the quartz surface more supersaturated with respect to hydrous Fe(III) oxides than the bulk solution, thus enabling nucleation on the quartz surface. Compared with growth/Ostwald ripening/aggregation, after a certain volume of hydrous iron oxide precipitates, more surface area of the hydrous iron oxides is generated in the nucleation dominant process.

In the presence of sulfate, useful information for identifying the dominant processes was obtained from DLS and AFM measurements. For particles homogenously formed in sulfate-containing solution, an extremely fast increase of the hydrodynamic particle size (from 243 ± 43 to 1868 ± 57 nm within 1 h, Figure 5.4B) was observed as we described in Section 3.1. The disappearance of electrostatic repulsive forces among neutrally charged hydrous Fe(III) oxide particles in solution significantly increased their probability of collision and attachment, leading to their fast aggregation and fast increase in the hydrodynamic particle size.

For the particles on the quartz surface after reaction in the sulfate solution, a broad range of primary nanoparticles (2–100 nm) (Figures 5.1D and 5.1E) as well as a very small amount of micro-sized aggregates were observed after the 1 hr experiment. The size of these micro-sized aggregates on the quartz surface was similar to the hydrodynamic particle size of the
homogeneously precipitated particles at the end of the 1 hr experiment; therefore, these aggregates may have formed in the bulk solution and attached to the quartz surface later upon collision. The big primary nanoparticle formation on the quartz surface is the result of fast growth. In both nitrate and chloride systems under our conditions, the hydrous Fe(III) oxide nanoparticle surfaces were positively charged (Table 5.1); while in sulfate system, the hydrous Fe(III) oxide particle surfaces were neutral ($\zeta = 0.3 \pm 0.6$ and $2.1 \pm 5.8$ mV, measured with and without the presence of quartz powder, respectively, Table 5.1). If we assume the hydrous Fe(III) oxide polymers in the presence of sulfate were also neutral, the removal of electrostatic repulsive force between the hydrous Fe(III) oxide particles and polymers can significantly increase the probability of collision between the particles and polymers, resulting in fast nucleation and growth. On the contrary, if we assume the hydrous Fe(III) oxide polymers in the nitrate and chloride systems were as positively charged as the particles, the electrostatic repulsive forces between the polymers and the particles would lower their collision chances, resulting in slower precipitation occurring in the nitrate and chloride systems than in the sulfate system. In the sulfate solution, once the particles formed on the quartz surface, their immobility and physical separation prevented them from fast aggregation. Thus, at the end of the 1 hr experiments, only a very small amount of micro-sized aggregates (Figure 5-S2) was observed on the quartz surface, which can be homogeneously precipitated particles that have attached to the quartz surface.

In previous studies of hydrous Fe(III) oxide precipitation in solution (without substrate), sulfate promotion of the Fe(III) precipitation$^{123}$ and aggregation$^{130}$ has been reported. Here, we provide the unique information that aggregation of the nanoparticles slowed down on the quartz substrate surfaces. Thus, fast growth was the dominant process for heterogeneous precipitation,
instead of fast aggregation for homogeneous precipitation. The result was big primary particles forming on the quartz surface, and even larger aggregates forming in solution.

5.4. Conclusions and Implications

This study provides qualitative and quantitative information about the location (i.e., in solution vs. on quartz surfaces), size, volume, number, and surface area evolutions of the hydrous Fe(III) oxide particles formed at acidic pH (pH = 3.7 ± 0.2) in the presence of nitrate, chloride, and sulfate. For both nitrate and chloride systems, the heterogeneously formed particles on quartz surfaces were smaller than their homogeneous counterparts. This difference shows the importance of heterogeneous precipitation for pollutant transport, because the smaller heterogeneously precipitated iron oxide nanoparticles have higher adsorption capacity due to higher reactivity and reactive surface area.\textsuperscript{120}

We also observed significantly less heterogeneous precipitation of hydrous Fe(III) oxides in the presence of chloride than nitrate. High chloride concentrations can exist in many aquifers such as at deep saline aquifers for CO\textsubscript{2} storage; the presence of chloride can influence the extent of immobilization of pollutants in these aquifers by adsorption to the precipitates on rock surfaces. Thus, we expect that, with high chloride concentration, heterogeneous precipitation of Fe(III) (hydr)oxide on mineral surfaces can be significantly inhibited. Thus, there will be a lower amount of aqueous pollutants immobilized through adsorption onto the heterogeneously precipitated iron oxides.

Furthermore, the dominant processes during the hydrous Fe(III) oxide precipitation, such as nucleation, growth, Ostwald ripening, and aggregation, were also found to be influenced by the presence of substrate and different anions. Possible mechanisms for the observed phenomena
were discussed, which provided the starting points for future molecular scale investigations on each detailed elemental mechanism. Other direct experimental probes at the interface, such as time resolved grazing incidence extended X-ray adsorption fine structure (GI-EXAFS) spectra, can complement our findings by providing detailed information on the molecular structure of the newly formed nanoparticles at the surface.

Finally, the information provided in this study can improve the accuracy of reactive transport modeling of the early stage precipitation process of hydrous Fe(III) oxides in the presence of anions abundant at GCS sites. Thus, it can be used to better predict the pollutant transport induced by CO₂ injection or CO₂ leakage.$^{131}$

**Acknowledgments**

This work was supported by a Washington University Faculty Start-up Grant and an NSF CAREER project (EAR-1057117). We would like to acknowledge Washington University’s Center for Materials Innovation (CMI) for use of HR-TEM. We thank Amy Miller and Dr. Soenke Seifert for experimental help, Dr. Alejandro Fernandez-Martinez for valuable discussion, and Dr. Matthew Suchomel for HR-XRD analysis of solid samples at APS Sector 11-BM. Use of the Advanced Photon Source (Sector 11-BM and 12ID-B) at Argonne National Laboratory was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.
Supporting Information for Chapter 5

Contents: Experimental and Data Analysis Details

Five figures (5-S1 – 5-S5)

Experimental Operation and Data Analysis Details

 Cleaning procedure for the quartz single crystals. To remove organic contaminants, the quartz pieces were sonicated in acetone for 10 minutes, and then soaked for 1 h in a highly concentrated sulfuric acid solution mixed with a commercial oxidizing agent, Nochromix. Finally, they were rinsed with ultrapure water (resistivity >18.2 MΩ-cm) and stored in micro-filtered distilled water.

 Solution preparation: All solutions (Table 5.1) were prepared with reagent grade Fe(NO₃)₃•9H₂O, NaNO₃, NaCl, and Na₂SO₄, and ultrapure water. Right before SAXS/GISAXS, DLS, or pH measurements, ultrapure water was added to the weighed salt (0.0452 g NaNO₃, 0.0292 g NaCl, or 0.0243 g Na₂SO₄) to make a final solution volume of 45 ml, and we shook the solution to mix it. Then, ultrapure water was added to 0.0202 g Fe(NO₃)₃•9H₂O to get a final solution volume of 50 ml, which we also quickly shook to mix. Finally, 5ml of this 10⁻³ M Fe(NO₃)₃ solution was added into the 45 ml salt solution, and the solution was shaken. So, the final solution contained 10⁻⁴ M Fe(NO₃)₃ and had an ionic strength of 10 mM. Because hydrous Fe(III) oxide precipitation started when the 10⁻³ M Fe(NO₃)₃ solution was prepared, timing started from this moment, and only 3 min elapsed before the first GISAXS image was taken.

 Preparing quartz powder in different acidic salt solutions. Quartz was ground to powder with a mortar and pestle, allowed to settle in each salt solution (NaNO₃, NaCl, or Na₂SO₄, all
with an ionic strength of 10 mM and pH around 3.7± 0.2, adjusted with HNO₃ for 10 min. Then, the upper region of the solution, which contained only small suspended quartz powder particles, was injected into a zeta cell for zeta potential measurements.

**Preparing precipitates for HRXRD.** To accumulate more precipitates for mineral phase identification, 500 ml of each of the solutions in Table 5.1 was prepared, and after 2 h, the solutions were centrifuged at 5000 rpm with Millipore Amicon ultra-15 centrifugal filter units. The precipitates that accumulated on the filters were collected on glass slides and dried in a desiccator for 2 h. Then, these precipitates were collected in Kapton® capillary tubes, stored at room conditions, and sent to ANL. Within 7 days, synchrotron-based high resolution X-ray diffraction (HRXRD) analysis, which requires only a small sample volume, was performed at sector 11-BM of APS in ANL. Both fast scan (3 min/sample) and slow scan (1 hr/sample) were performed. No difference was observed, indicating no X-ray induced artifact.

**Invariant calculations.** In the definition of invariant Q, the integration region over q is infinite; however, during our SAXS/GISAXS measurements, only a certain q range could be measured. In both nitrate and chloride systems, the Lorentz-corrected GISAXS intensities (Figure 5.3A1 and 5.3A2) at both bounds of the measured q range are close to zero, indicating that the integration over the measured q range represents the total volume of the particles that precipitated on the quartz surfaces. For particles formed in these solutions, extrapolations were conducted in the Lorentz-corrected intensity plots, as indicated by the dashed lines in Figures 5.3B1 and 5.3B2, to get the total particle volume. The big particles formed in the presence of sulfate were out of the measurement range of GISAXS/SAXS; thus, we could not calculate the invariants.
The evolutions of the GISAXS invariants calculated between triplicate runs were very consistent, as indicated by the small error bars in Figure 5.4A. The evolutions of the SAXS invariants fluctuated within the range indicated by the box in Figure 5.4A. Several reasons could have caused the large fluctuation of the SAXS invariants: the particles in these solutions were larger than those formed on quartz surfaces, and fewer particles in these solutions were hit by X-ray than those on quartz surfaces. Also, the particles can move around in solutions.

**Primary particle size, total volume, number and surface area calculations.** The evolutions of the relative total volumes of particles detected by X-ray scattering were calculated using the definition of invariant (Figure 5.4A). The 1D scattering curves were fit to eqn. (1), where \( P(q, r, \sigma) \) is the form factor, and \( S(q, I_{\text{os}}, d, R_h, v_f) \) is the structure factor.

\[
I(q) = I_0 P_0(q, r_0, \sigma_0) S(q, I_{\text{os}}, d, R_h, v_f) + I_1 P_1(q, r_1, \sigma_1)
\]  

(1)

\[
P(q, R, \sigma) = (\Delta \rho)^2 \int n(R, \sigma) V^2 \frac{9(\sin(qR) - qR \cos(qR))^2}{(qR)^6} dR
\]  

(2)

\[
S(q, I_{\text{os}}, d, R_h, v_f) = I_0 q^d + S(q, R_h, v_f)
\]  

(3)

For the form factor \( P(q, r, \sigma) \), a polydisperse sphere model with the Schultz distribution as a size distribution function was used, as shown in eqn. (2). \( n(R, \sigma) \) is the Schultz distribution function used to represent the observed size polydispersity of the particles.\(^{139}\) A spherical model was used because when the size distribution is broad and no form factor oscillation is found in the scattering curves, the shape of particles is hard to resolve unless they are highly anisotropic. Thus, the shape of particles is approximated to a low-resolution, highly symmetric shape, such as a sphere. \( \Delta \rho \) is the electron density difference between the nanoparticles and solutions, and \( V \) is the particle volume.
For the particles precipitated on the quartz surface in the presence of nitrate, an additional peak was observed on the Lorentz-corrected GISAXS curves in the later stage (Figure 5.3A1), indicating the presence of a bimodal particle size distribution. Thus, the 1D scattering curves (Figure 5.2A1) were fit to a polydisperse sphere model with the bimodal Schultz distribution as the size distribution function. \( P_0 \) and \( P_1 \) respectively denote the large particles formed from the early stage and the small 1 nm particles formed in the later stage. For the particles precipitated on the quartz surface in the presence of chloride, only one peak was observed on the Lorentz-corrected GISAXS curves. Thus, \( I_1 \) was set as 0. The larger particles showed interparticle distance peaks and a power law behavior in the low q range, which can be modeled by the structure factor, \( S(q, I_{os}, d, R_h, v_f) \) as shown in eqn. (3). Here \( S(q, R_h, v_f) \) represents the hard-sphere Percus-Yevick model, with \( R_h \) and \( v_f \) being the hard-sphere interaction distance and the volume fraction, respectively. The detailed equations for this model are provided in the book written by Lindman and Alexandridis.\(^{149}\) The smaller particles are well dispersed, and therefore the structure factor function is not required for them.

The fitted values of \( r \) and \( \sigma \) after reaction for different times were used to calculate the evolution of the average radii of gyration (\( R_g \)) of the primary particles, according to the Schultz distribution function (Figure 5.4B). For the particles precipitated on the quartz surface in the presence of nitrate, two primary particle sizes and their relative total particle volumes were obtained after the fitting. Then, the total primary particle number and surface area were calculated as the sum of the particles with the two different sizes. Using the spherical particle assumption for the calculation of individual particle volumes, given the total particle volumes (Figure 5.4A) and the average primary particle sizes (Figure 5.4B), the total primary particle
numbers (Figure 5.4C) and surface areas (Figure 5.4D) were calculated. All data analysis was performed with the Igor Pro program (V. 6.22A, WaveMetrics, Inc., Oregon).

Comparison of the volumes of homogeneously and heterogeneously precipitated particles.

In this study, throughout the 2 hr experiments, in nitrate system, for the heterogeneously and homogeneously precipitated nanoparticles detected by X-ray, the ratios of the total particle volumes were around 42.6 ± 16.5. In our previous study conducted with the presence of nitrate, the ratio of heterogeneously to homogeneously precipitated iron oxide nanoparticles detected by X-ray after 1.1 hr reaction time was 192:1,\(^4\) higher than the ratio (42.6:1) observed here. In the previous study, (100) surface of quartz was used. Based on our preliminary test, the (100) surface of quartz is more reactive than the (102) surface of quartz used in this study, which might have caused the difference.

During simultaneous homogeneous and heterogeneous precipitation, the ratio of the solution volume and the exposed surface area can affect the ratio of the total volumes of the particles precipitated in solution and on the substrate surface. To calculate the total particle volume formed in the entire solution volume and on the entire quartz surface, we considered the geometry of the SAXS/GISAXS experimental setup and calculated the percentages of the particles detected by X-ray during the experiments. The geometry of the quartz surface exposed to solution was 1 cm × 1 cm, and the geometry of the solution was 1 cm × 1 cm × 1 cm, resulting in a 1 cm\(^2\) quartz surface exposed in 1 ml solution. The X-ray beam size was 100 μm × 100 μm; thus, 1% (1cm×100μm) of the entire surface of the quartz was hit by X-ray during GISAXS measurement, and a 0.01% volume of solution (1cm×100μm×100μm) was hit by X-ray during SAXS measurement. Normalizing the total volumes of the particles detected by X-ray (Figure 5.4A) with their percentages to the total particles formed under the experimental conditions,
throughout the 2 hr experiments, the ratios of the total volumes of the heterogeneously precipitated particles on 1 cm$^2$ quartz surfaces over the homogeneously precipitated particles in 1 ml solutions were around 0.43 ± 0.16 and 0.06 ± 0.02, in the presence of nitrate and chloride, respectively. In natural reservoirs, small quartz grains generate a much larger surface area exposed to solution than the single quartz crystal used in our experiments. With a higher ratio of exposed substrate surface area over the fluid volume, a higher ratio of the total volume of heterogeneously precipitated particles over homogeneously precipitated particles can be expected.

We also considered the deposition of the homogeneously precipitated particles on the quartz surface. Once the particles formed in solution, it is possible that they could deposition the quartz surface by electrostatic forces. However, their contribution is insignificant compared to the total particles observed on the quartz surface. Because if both deposition of homogeneously precipitated particles and heterogeneous precipitation are dominant processes for particle formation on the quartz surface, we should have observed abundant particles with two different sizes on the quartz surface, owing to different sizes of particles from the two mechanisms. However, based on AFM observations (Figure 5-S5), only a few big particles (10-20 nm, indicated by the arrows in the AFM images) were observed on the quartz surfaces, while many small particles were all over the quartz surfaces. The smaller particles were formed through heterogeneous precipitation. The size of the bigger particles matched well with the sizes of the homogeneously precipitated particles in solution. They were thought to have formed in solution through homogeneous precipitation and later attached to the surface. As shown in the images, the contribution of the big homogeneously precipitated particles on the quartz surface is insignificant compared to those of the heterogeneously precipitated particles.
Figure 5-S1. GISAXS/SAXS geometry. During the measurement, the scattered X-ray was measured on the 2-D detector; meanwhile, a portion of the incident beam was transmitted through the solution and hit the photodiode. Before analyzing any scattering data, we carefully examined the photodiode values, and confirmed that no significant sample or beam movement happened during the measurement. For GISAXS measurement, a small incident angle $\alpha_i$ (the angle between the incident X-ray beam and the substrate surface) of 0.13° was chosen (98% reflectivity at 12 keV). With this incident angle, the X-ray beam probed only structures on the substrate surface.
Figure 5-S2. Large aggregates on the quartz surface after reaction in $10^{-4}$ M Fe$^{3+}$ solutions with 3.42 mM Na$_2$SO$_4$. 
Figure 5-S3. HRXRD patterns of the precipitates formed in solution. The XRD peaks of the particles formed in nitrate and chloride solutions match well with the reference of ferrihydrite, as indicated by the black dashed lines. In the sulfate system, the XRD peaks of the particles match well with the reference of schwertmannite, indicated by the blue dashed lines.
Figure 5-S4. Variations of solution pH over time.
**Figure 5-S5.** AFM tapping mode observations of the quartz surfaces after reaction in nitrate (A) and chloride (B) solutions for 2 h.
Chapter 6. Control of Heterogeneous Fe(III) (Hydr)oxide Nucleation and Growth on Quartz, Mica, and Sapphire by Interfacial Energies and Local Saturations

Results of this Chapter have been submitted to *Environmental Science and Technology*

Abstract

To predict the fate of aqueous pollutants, a better understanding of heterogeneous Fe(III) (hydr)oxide nucleation and growth on abundant mineral surfaces is needed. In this study, we measured *in situ* heterogeneous Fe(III) (hydr)oxide nucleation and growth on quartz, muscovite, and sapphire (Al$_2$O$_3$) in $10^{-4}$ M Fe(III) solution (in 10 mM NaNO$_3$ at pH = 3.7 ± 0.2) using grazing incidence small angle x-ray scattering (GISAXS). Interestingly, both the fastest heterogeneous nucleation and slowest growth occurred on sapphire. To elucidate the mechanisms, zeta potential and water contact angle measurements were conducted. Electrostatic forces between the charged Fe(III) (hydr)oxide prenucleation clusters (PNCs) and substrate surfaces—which affect local saturations near the substrate surfaces—controlled heterogeneous growth rates. Water contact angles (7.5° ± 0.7, 22.8° ± 1.7, and 44.8° ± 3.7 for quartz, muscovite, and sapphire, respectively) indicate a highest substrate-water interfacial energy for sapphire. Further, comparison of structural mismatches between the substrates and precipitates indicates a lowest precipitate-substrate interfacial energy for sapphire. The fastest nucleation on sapphire suggests that interfacial energies in the solution–substrate–precipitate system controlled heterogeneous
nucleation rates. The unique information provided here bolsters our understanding of nanoparticle-mineral interactions, mineral surface modification by iron oxide coating, and pollutant transport.

6.1 Introduction

The heterogeneous nucleation and growth of Fe(III) (hydr)oxides on mineral surfaces are important processes in natural and engineered aquatic systems. Often Fe(III) (hydr)oxides precipitate on other rocks’ surfaces via heterogeneous nucleation, and change the reactivity of the pre-existing rocks, which may previously have low sorption capability for pollutants.\textsuperscript{147, 148, 151} During heterogeneous Fe(III) (hydr)oxide precipitation, organic ligands,\textsuperscript{134} heavy metals (Cu, Zn, Pb, Cr, Ni, Cd, Mo, V, etc.),\textsuperscript{152-154} and arsenic\textsuperscript{155-160} can be immobilized on mineral surfaces through adsorption and coprecipitation processes.\textsuperscript{120, 121, 160} This immobilization process has been reported at field sites for acid mine drainage,\textsuperscript{161-163} managed aquifer recharge,\textsuperscript{164} and geologic CO\textsubscript{2} sequestration.\textsuperscript{6, 20} For example, at the Frio-I Pilot GCS site (Gulf Coast, USA),\textsuperscript{6, 20} after CO\textsubscript{2} injection, the pH decrease caused the increase in dissolved Fe concentration (30-1100 mg/L) and the release of heavy metals, including Zn and Pb, which were originally adsorbed to the iron (hydro)oxides.\textsuperscript{20} The mobilization of these pollutants could have severe environmental impacts if they migrated into potable groundwater (for example, during CO\textsubscript{2} leakage).\textsuperscript{20} As the acidic brine was neutralized during its flow, Fe reprecipitation occurred. To study the possible pollutant transport caused by CO\textsubscript{2} injection or leakage, accurate precipitation kinetic data of iron (hydro)oxides, especially for heterogeneous precipitation, are desired.
To predict the Fe(III) (hydr)oxide precipitation and the transport of aqueous pollutants in field sites, reactive transport models can be used. In these models, the rate of mineral precipitation from aqueous solution can be written as follows:\textsuperscript{131}

\[ Rate = Akf(\Omega) = Akf(Q/K) \] (1)

where \( k \) is the rate constant, and \( f(\Omega) \) is a function of the saturation ratio (\( \Omega \)), which is the ratio between the actual dissolved compositions (\( Q \)) and the corresponding equilibrium compositions (\( K \)). The mineral surface area (\( A \)), which is a function of the number and size distribution of the precipitates, is initially created by nucleation and modified by both nucleation and growth. Because of limited experimental data on nucleation and growth kinetics, the mineral surface area is in general the least accurate parameter in reactive transport modeling.\textsuperscript{131} This inaccuracy significantly hinders better prediction of Fe(III) (hydr)oxide precipitation. In addition, the adsorption capacities of Fe(III) (hydr)oxide nanoparticles for pollutants are strongly size-dependent.\textsuperscript{165, 166} Heterogeneous nucleation and growth rates of Fe(III) (hydr)oxide can affect both the sizes of the precipitates and their distributions among different mineral surfaces. Thus, to better predict pollutant transport, it is crucial to measure these rates on environmentally abundant mineral surfaces.

Quartz (\( \text{SiO}_2 \)), muscovite (white mica, \( \text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH,F})_2 \)), and sapphire (\( \text{Al}_2\text{O}_3 \)) are abundant minerals in the earth’s crust. The chosen crystal planes differ in surface structures (details in Figure 6-S1 in Supporting Information), pH\textsubscript{iep} values,\textsuperscript{167} and hydrophobicity/hydrophilicity properties. These surface properties can affect the interactions (e.g., electrostatic forces, adsorption, and bond formation) between these surfaces and the local aqueous species.\textsuperscript{168-170} Therefore, the local saturation ratio (\( \Omega \)) near these substrate surfaces can
differ from that of the bulk solution.\textsuperscript{69, 106, 168, 171} The diverse surface properties of these minerals can also affect the interfacial energies within the solution–substrate–precipitate system.\textsuperscript{171, 172} Thus, it is important to quantify the different heterogeneous nucleation and growth rates of Fe(III) (hydr)oxide on these surfaces, and to identify the controlling mechanisms.\textsuperscript{109, 131} Until now, the heterogeneous nucleation and growth rates of Fe(III) (hydr)oxide on these mineral surfaces have not been clearly quantified and compared due to the technical difficulty in probing the heterogeneously precipitated nanoparticles \textit{in situ} at the mineral–water interface.

In this study, we aimed to fill this important information gap. Our previously developed grazing incidence small angle X-ray scattering (GISAXS) setup was employed to quantify \textit{in situ} size and volume evolutions of Fe(III) (hydr)oxide nanoparticles precipitated at substrate/liquid interfaces,\textsuperscript{168, 171} and compare the heterogeneous nucleation and growth rates on different substrates. To elucidate the controlling mechanisms, the physico-chemical and structural properties of the nanoparticles and the substrates were characterized with complementary techniques, including electrophoretic mobility, contact angle measurements, high resolution transmission electron microscopy (HRTEM), and X-ray diffraction (HRXRD).

6.2. Materials and Methods

6.2.1 Substrate and Solution Preparation

We purchased synthetic single crystal quartz (Princeton Scientific Co.), muscovite (Goodfellow Cambridge Limited), and sapphire (MTI Corporation). Quartz (102) surfaces, muscovite (001) surfaces, and sapphire (0001) surfaces (C-plane) were chosen in this study based on their natural abundance and broad industrial applications.\textsuperscript{69, 70, 106, 173-181} For example, the muscovite (001) surface, abundant in natural environments, is structurally similar to the
dominant surfaces of many clay minerals. In addition, the ease of perfect cleavage along the muscovite (001) plane and its availability in high-grade natural and synthetic forms makes it a favorite substrate for epitaxially grown metal and crystal layers in diverse fields. All the samples used had atomic flat surfaces (AFM images in Figure 6-S2). By utilizing high quality synthetic samples with well-cut surfaces, a more complete and less ambiguous interfacial reaction characterization could be accomplished. All samples were cut into 1 cm × 1 cm squares to fit into the GISAXS/SAXS cell and were cleaned before measurements, as described in the Supporting Information.

To prepare a $10^{-4}$ M Fe$^{3+}$ solution with 10 mM ionic strength, we used reagent grade Fe(NO$_3$)$_3$, NaNO$_3$, and ultrapure water. The measured pH values of the solution throughout the experiments were $3.7 \pm 0.2$. Using the log $K$ value of -7.22 at 20 ºC, the saturation index (SI = log (Q/K) = log Ω) with regard to Fe(OH)$_3$ was calculated to be 0.2, using Geochemist’s Workbench (GWB, Release 8.0, RockWare, Inc.).

6.2.2 In Situ GISAXS Measurements

At 12 keV X-ray energy, an incident angle of 0.13° was chosen. At this incident angle, the X-ray probed only the structures at the substrate surfaces, and the calculated reflectivities of quartz, muscovite, and sapphire were similar (with densities of 2.65, 2.82, and 3.99 g/cm$^3$, the calculated reflectivities were 97.9%, 98.0%, and 98.7%, respectively). For each in situ run, a fresh 1 cm × 1 cm square substrate was placed inside a specially designed SAXS/GISAXS fluid cell, and the top surface of the substrate was aligned with the middle of the X-ray beam. The in situ run started as soon as 1 ml of freshly mixed solution was injected into the GISAXS cell. Only 2 minutes elapsed before the first GISAXS image was taken. During the run, time-resolved scattering signals were collected from particles precipitated on the substrate at 30 s
intervals. Meanwhile, incident and transmitted X-rays were detected by the ionic chamber (IC) and photodiode, respectively. The geometry of the GISAXS measurements and more details can be found in our previous studies.\textsuperscript{42,168} Experiments were conducted at beamline 12 ID-B at the Advanced Photon Source (APS), Argonne National Lab (ANL), IL.

### 6.2.3 GISAXS Data Analysis

First, the IC and photodiode values measured were examined carefully to confirm that the X-ray beam intensity was stable and the alignments were good throughout all measurements. Thus, the differences in the scattering intensities came from the sample, not the X-ray beam’s condition. Triplicate experiments were run for quartz, mica, and sapphire, and consistent results were obtained.

Second, for each experiment set, the first 2D scattering image was used as the background and was subtracted from each following 2D image; then, the subtracted 2D image was reduced to 1D by doing line-cuts along the Yoneda wing, where the scattering signal is enhanced along the in-plane direction due to the grazing incidence effect in GISAXS.\textsuperscript{136,137} Figure 6.1 shows the GISAXS scattering intensities (I) plotted against the scattering vector q (unit: Å\textsuperscript{-1}) from particles precipitated on the substrate surfaces.

Next, the GISAXS 1D scattering curves (Figure 6.1) were fit to the polydisperse sphere model with a structure factor included. Schultz distributions were used to get the particle size distributions, and the radii of gyration (R\textsubscript{g}) of the particles were calculated (Figure 6.2A).\textsuperscript{139} The invariant \( Q \),\textsuperscript{138} which is defined as \( Q = \int_0^\infty I(q)q^2dq \) and is proportional to the total volumes of precipitated nanoparticles (V, Figure 6.2B), was also calculated based on the fitted curves. Assuming a spherical particle shape and using the total particle volumes (V, Figure 6.2B) and
average particle sizes ($R_g$, Figure 6.2A), the total particle numbers (N, Figure 6.2C) were calculated in relative units: $N = V/R_g^3$. GISAXS data reduction was performed with the GISAXS-SHOP macro, available at APS beamline 12 ID. All data analysis was performed with the Igor Pro program (V. 6.22A, Wave Metrics, Inc., Oregon).

### 6.2.4 Atomic Force Microscopy, Zeta Potential ($\zeta$), and Contact Angle Measurements

As a supplement to the *in situ* GISAXS measurements, *ex situ* atomic force microscopy (AFM) measurements were conducted after the GISAXS experiments, to observe the precipitates on the substrate surfaces. AFM tapping mode (Veeco Inc.) was used, to collect height, amplitude, and phase images simultaneously. Probes were 125 μm long with phosphorus (n) doped silicon tips (MPP-11100-10, Veeco probes). Images were collected with drive frequencies between 312–320 kHz, typical spring constants of 20–80 N/m, and a scan rate of 0.80 Hz. Nanoscope 7.20 software was used to analyze topographic features.

A Zetasizer instrument (Nano ZS, Malvern Instruments Ltd.) was used for zeta potential and hydrodynamic particle size measurement. Freshly mixed solution was injected into a zeta cell (DTS1060C, Malvern Instruments), and the zeta potentials of the Fe(III) (hydr)oxide precipitates were measured every minute for 1 h at 20 °C. Because of the technical difficulty in measuring zeta potentials of single crystal surfaces, zeta potentials of quartz, mica, and sapphire powders were measured at our experimental conditions (pH = 3.7 ± 0.2 in 10 mM NaNO$_3$ solution).

Water contact angles on the surfaces were measured in air using a Phoenix 300 instrument (Surface Electro Optics Co. Ltd, Korea). Each surface was placed on a horizontal holder and brought into contact with a water droplet hanging from a vertical needle connected to a syringe.
Video acquisition was performed using a CCD camera, and 10 sequential measurements of the contact angles were conducted using a goniometer within 10 s of when the droplet touched the surface. Triplicate samples were measured.

6.2.5 Precipitate Phase Identification

To identify the phases of the precipitates on the substrates, first, Raman spectroscopy data were recorded using a Raman microscope (Renishaw, U.K.) with 633 nm excitation wavelength; however, no peaks except those from the substrates were detected. Second, we took off the precipitates from the substrates by sonicating them in ethanol. Then, a drop of this suspension was placed on a Formvar/carbon-coated Cu grid and dried overnight in a desiccator. Electron diffraction measurements were performed for the nanoparticles on the grid using HRTEM (JEOL JEM-2100F field emission); however, no diffraction patterns were obtained, indicating the precipitates were amorphous. To facilitate phase identification, the homogeneous precipitated particles were collected by centrifuging. HRXRD analysis was conducted after a 7-day aging, and broad peaks of ferrihydrite were observed. Based on all this information and our previous experiments with grazing incidence wide angle X-ray scattering (where no diffraction peak was found), we concluded that the precipitates formed on the substrates were poorly crystallized Fe(III) (hydr)oxides.

6.3. Results

6.3.1. Size and Relative Total Volume Quantification of the Precipitates on Substrates

GISAXS scattering intensities from precipitates on different substrate surfaces are plotted (Figures 6.1A-C) against the scattering vector \( q (\text{Å}^{-1}) \) at different reaction times. The shapes of
the scattering intensity curves are related to the particle sizes, while the scattering intensities correlate to the total amounts of particles on the substrate surfaces. Interestingly, these curves show that for the same aqueous condition, the heterogeneously precipitated Fe(III) (hydr)oxide nanoparticles on different mineral surfaces varied in terms of both size and total amount of particles, indicating that the heterogeneous nucleation and growth of Fe(III) (hydr)oxides were significantly influenced by substrate identity.

**Figure 6.1.** GISAXS scattering intensities cutting along the Yoneda wing from particles on quartz (A), mica (B), and sapphire (C) surfaces immersed in $10^{-4}$ M Fe$^{3+}$ solutions with 10 mM NaNO$_3$. The black lines show the fitted curves. The *in situ* GISAXS/SAXS experiments were conducted at 20 ºC for 1 h. Throughout the experiments, water evaporation was very slow and no significant volume change of the original 1 ml solution occurred.

As indicated by the orange arrows in Figure 6.1, as the reactions continued, the peak positions of the scattering intensity curves shifted to lower q. Since q is reciprocally related to particle size, these peak shifts indicate increases in particle sizes. To get more accurate particle sizes, the scattering curves (Figures 6.1) were fitted with the polydisperse sphere model with a structural factor included, and the average radii of gyration ($R_g$) of the particles were calculated (Figure 6.2A). Particle size fitting was not performed for quartz, mica, and sapphire until 7, 20,
and 9 min, respectively, because the low X-ray scattering intensities early in the reactions were insufficient to obtain good fitting. At the end of 1 h experiments, the \textit{in situ} average radii of the particles were 6.2 ± 0.3, 4.9 ± 0.5, and 3.8 ± 0.2 nm on quartz, mica, and sapphire, respectively. The fitted average particle sizes on mica had a relatively large error because of the low intensity data obtained. \textit{Ex situ} AFM measurements conducted on dry samples showed 2–4 nm particles (Figures 6.3A-C), which were slightly smaller than the sizes measured by \textit{in situ} GISAXS at the end of the 1 hr experiments (4~6 nm). This difference could be due to dehydration of the \textit{ex situ} samples.

![Graphs showing particle size, total volume, and particle number over time](image)

**Figure 6.2.** Evolutions of average radii (A) and the total volumes (B) and numbers (C) of the nanoparticles precipitated on the substrate surfaces from 10^{-4} M Fe^{3+} solutions with 10 mM NaNO_3.

Based on invariant calculations from the fitted curves (Figure 6.1), the evolution of total particle volumes (V, in relative units) on the substrate surfaces are plotted over reaction time (t) in Figure 6.2B. The slopes of the curve, which represent increases in total particle volume per unit time and reflect both nucleation and growth, were defined as the precipitation rates. During the first 20 min, faster precipitation occurred on quartz than on sapphire. Later on, faster precipitation occurred on sapphire than on quartz. The slowest precipitation occurred on mica,
where the data intensities were too low to analyze until 20 minutes had elapsed. At the end of the 1 hr experiments, the total particle volumes on quartz and sapphire were similar, and were around 4 times higher than on mica.

A. (102) surface of quartz  B. (001) surface of mica  C. (0001) surface of \( \alpha \)-\( \text{Al}_2\text{O}_3 \)

**Figure 6.3.** *Ex situ* AFM observations of quartz (A), mica (B), and sapphire(C) surfaces after reactions. The typical lateral resolution of the tapping mode used here was ~ 40 nm, which is much bigger than the real particle sizes, while the vertical resolution was sub angstrom. Thus, the real particle sizes were measured accurately in the vertical direction, which are quantified by the line cut curves below the images.

### 6.3.2. Surface Charges of the Precipitates and the Substrates

To understand the electrostatic interactions between the surfaces and the aqueous species, zeta potential measurements (\( \zeta \), Table 6.1) were conducted. The hydrous Fe(III) oxides precipitates (\( \zeta = 35.1 \pm 4.0 \) mV) and the sapphire powder (\( \zeta = 41.7 \pm 6.3 \) mV) were positively charged, while the quartz (\( \zeta = -14.3 \pm 2.6 \) mV) and mica (\( \zeta = -17.3 \pm 4.2 \) mV) powders were negatively charged.
Table 6.1 Measured zeta potential ($\zeta$) values with powder samples and reported pH_{iep} of different substrates.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>$\zeta^*$ (mV)</th>
<th>pH_{iep}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxides</td>
<td>35.1 ± 4.0</td>
<td>6.8–8.1 (ferrihydrite)</td>
<td>151, 154, 167,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.5–9.5 (hematite)</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>184, 185</td>
</tr>
<tr>
<td>Quartz</td>
<td>-14.3 ± 2.6</td>
<td>2.0–3.0</td>
<td>151, 167, 186,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>187</td>
</tr>
<tr>
<td>Muscovite</td>
<td>-17.3 ± 4.2</td>
<td>always negative</td>
<td>67, 188</td>
</tr>
<tr>
<td>Sapphire</td>
<td>41.7 ± 6.3</td>
<td>8–10 (powder)</td>
<td>167, 189, 190,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5–7 (crystal plane)</td>
<td>191-193</td>
</tr>
</tbody>
</table>

Note: "The zeta potential values were measured with quartz, mica, and sapphire powders under our experimental conditions (i.e., in 10 mM NaNO\textsubscript{3} with pH adjusted to 3.7 using HNO\textsubscript{3}).

The pH_{iep} values of different substrates are cited from references. The basal surface of muscovite is always negatively charged, thus, no pH_{iep} value is applied.

Our zeta potential measurements agree well with surface charges expected from the reported pH_{iep} values of these minerals. As listed in Table 6.1, the pH_{iep} values for iron oxides\textsuperscript{151, 154, 167, 183-185} and quartz\textsuperscript{151, 167, 186, 187} are reported as 6.8–9.5 and 2.0–3.0. The pH_{iep} values for sapphire are reported to be in the range of 8–10 for powders\textsuperscript{167, 189, 190} and 5–7 for the single crystal planes\textsuperscript{191-193} (Table 6.1). Thus, based on these reported pH_{iep} values, at our experimental pH (3.7 ± 0.2), the iron oxides and sapphire, which have pH_{iep} values higher than the experimental pH condition, should be positively charged. Quartz, which has a pH_{iep} value lower than the experimental pH condition, should be negatively charged. For the (001) plane of muscovite, the Si/Al tetrahedral layer was exposed. Because of the isomorphic substitution of
tetravalent silicon (Si$^{4+}$) by trivalent aluminum (Al$^{3+}$), this surface has a permanent negative structural charge, and its surface charge is independent of pH.\textsuperscript{170, 67, 170, 194, 195}

Considering the potential differences in zeta potential values between powder samples and single crystal surfaces, we consulted the reported surface charges of these single crystal surfaces. For the (0001) plane of sapphire, a zeta potential of 18 ± 3 mV at pH = 3.7 was measured by streaming potential technique.\textsuperscript{196} Quartz single crystal surfaces were found to be negatively charged at pH 3.7, using both streaming potential measurement and XPS spectra calculation.\textsuperscript{197} These reported surface charges of quartz and sapphire single crystals agree with our powder measurements in terms of being positive or negative, although the absolute values may differ.

6.3.3. Water Contact Angles on Substrates and Their Relation to Substrate–Water Interfacial Energies

To elucidate the role of the interfacial energy barrier on heterogeneous nucleation, we considered the substrate–water interfacial energies; however, there are only a few reported values in the literature, and these values are not very consistent with each other. For example, quartz–water interfacial energy (σ$_{\text{quartz-water}}$) values of 360, 340, 120, and 416 mJ/m$^2$ have been reported.\textsuperscript{198-201} Such inconsistency may be caused by the different treatment of these substrate surfaces or by different measuring methods, as the substrate–water interfacial energy can be affected by many factors, such as the surface roughness and coating, as well as the cleaning procedures.

To obtain consistent data for comparison between substrate surfaces used in this study, water contact angles on these substrates were measured in air. Substrates utilized were the same quality and were cleaned following the same procedures as in GISAXS experiments. The water contact angles of the substrates measured in air were 7.5° ± 0.7, 22.8° ± 1.7, and 44.8° ± 3.7 for
quartz, muscovite, and sapphire, respectively. For less hydrophilic surfaces, they have larger water contact angles, would also have higher substrate–water interfacial energies (σ_{substrate-water}). Therefore, we determined a semi-quantitative ranking of these interfacial energies to be

σ_{quartz-water} < σ_{mica-water} < σ_{sapphire-water}.

### 6.4. Discussion

#### 6.4.1. Defining the Nucleation and Growth Rates during Fe(III) (hydr)oxide Precipitation

Before comparing the nucleation and growth rates on the substrates and exploring the mechanisms, we considered the pathways of Fe(III) (hydr)oxide precipitation. The first step is hydrolysis of ferric ion to form the monomer (eqn. 2), followed by polymerization through continuous olation(hydroxo–bridging) and oxolation(oxo–bridging) reactions (eqn. 3 and 4). Once the size of the polymer, also called the prenucleation cluster (PNC), is larger than the critical size, the PNC becomes thermodynamically stable and is termed a nucleus. From there, further growth can occur by addition of PNCs to the nuclei.

**Hydrolysis:** Fe^{3+} + 3 H_{2}O \rightarrow Fe(OH)_{3} + 3 H^{+} \quad (2)

**Olation:** 2[Fe(H_{2}O)_{3}OH^{2+}] \rightarrow [(H_{2}O)_{4}Fe-(OH)_{2}-Fe(H_{2}O)_{4}]^{4+} + 2H_{2}O \quad (3)

**Oxolation:** 2[Fe(H_{2}O)_{5}OH^{2+}] \rightarrow [(H_{2}O)_{4}Fe-O-Fe(H_{2}O)_{5}]^{4+} + H_{2}O \quad (4)

Once stable nuclei form, Fe(III) (hydr)oxide precipitation begins. From then on, as continuous nucleation and growth occur, the number and size of the precipitates will vary accordingly. Nucleation, which creates new stable nuclei from solution, increases the particle number while maintaining the particle size. Since particles are generated through nucleation only,
thus, the particle numbers represent the nucleation rates. On the other hand, during the growth process, Fe(III) (hydr)oxide PNCs in solution attach to the existing particles. Therefore, the particle size increases while the particle number remains constant. As observed by AFM (Figure 6.3), the heterogeneously precipitated particles on the substrates are individual particles, rather than continuously grown films. Thus, the heterogeneous growth rate is defined as the increase in particle size per unit time. Based on these definitions, in the following Sections 4.2 and 4.3, the heterogeneous nucleation and growth rates on the substrates are compared and potential mechanisms are discussed.

6.4.2. Comparatively Slow Heterogeneous Growth on Sapphire: Role of Electrostatic Forces

To compare the heterogeneous growth rates on the substrates, linear regressions (black lines in Figure 6.2A) were conducted for the average particle size ($R_g$) evolutions over reaction time ($t$). The linear relationships are $R_{g_{\text{quartz}}} = 0.6 \ t + 2.6 \ (R^2 = 0.96)$, $R_{g_{\text{mica}}} = 0.6 \ t + 1.3 \ (R^2 = 0.91)$, and $R_{g_{\text{sapphire}}} = 0.4 \ t + 1.4 \ (R^2 = 0.93)$. Based on the slopes of these regressions, the heterogeneous growth rates (unit: nm/min) of Fe(III) (hydr)oxide nanoparticles on mica and quartz were similar considering the error range, and both were faster than on sapphire.

The heterogeneous growth process requires the diffusion and attachment of PNCs in solution to the existing particles on the substrate surfaces. Thus, the local saturation ratio ($\Omega$), which can be defined as the local concentration of PNCs divided by the equilibrium concentration, is the driving force for heterogeneous growth. Higher concentrations of Fe(III) (hydr)oxide PNCs in the local solution near the surfaces promote faster heterogeneous growth. Because the bulk solutions were identical for all experiments using different substrates, to
explain the different heterogeneous growth rates, we evaluated the different substrate surface properties which could affect their local solution compositions.

First, electrostatic forces between the substrate surfaces and the aqueous ions were considered. As shown in eqn. (2), the hydrolysis reactions produce Fe(III) (hydr)oxide monomers as the prerequisite for PNC formation. The hydrolysis reaction is promoted by high \( \text{Fe}^{3+} \) and low \( \text{H}^+ \) concentrations. Therefore, to have high local PNC concentrations, high local \( \text{Fe}^{3+} \) and low \( \text{H}^+ \) concentrations are preferred. As discussed in Section 3.2, quartz and mica surfaces were similarly negatively charged, while sapphire was positively charged. Considering this effect on the local distributions of aqueous ions, the aqueous cations (Na\(^+\), H\(^+\), and Fe\(^{3+}\)) would be attracted towards the mica and quartz surfaces, while the anions (OH\(^-\), NO\(_3^-\)) would be attracted to the sapphire surfaces. Considering only the electrostatic forces and not the surface adsorption of specific ions, a high local \( \text{Fe}^{3+} \) concentration requires a negatively charged surface, while a low \( \text{H}^+ \) concentration requires a positively charged surface. Therefore, a high local \( \text{Fe}^{3+} \) and a low \( \text{H}^+ \) concentration cannot be achieved at the same time for either positively or negatively charged surfaces. Thus, the effects of the electrostatic forces between the charged surfaces and aqueous cations and anions on the local Fe(III) (hydr)oxide monomer concentration offset each other.

Second, we considered the electrostatic forces between the substrate surfaces and the Fe(III) (hydr)oxide PNCs in solution, which can affect the local PNC concentrations near the substrate surfaces, thus affecting the local saturations. If we assume the Fe(III) (hydr)oxide PNCs in solution were as positively charged as the Fe(III) (hydr)oxide particles (Table 6.1), there should be similar electrostatic attractive forces between the PNCs in solution and the quartz and mica surfaces, while electrostatic repulsive forces exist between the PNCs and the sapphire surface.
Given this, the slowest growth should occur on sapphire, and similar growth rates should occur on quartz and mica surfaces, as observed in our experiments. This agreement suggests that the electrostatic forces between the charged PNCs and the surfaces, which affect the local saturations, control the heterogeneous growth rates.

6.4.3. The Comparatively Fast Heterogeneous Nucleation on Sapphire: Role of Interfacial Energies

The calculated particle numbers (Figure 6.2C) on the substrates were used to compare the relative heterogeneous nucleation rates. The particle numbers on sapphire increased with time (indicated by the guideline in Figure 6.2C) and were the most among the three substrates, indicating the fastest nucleation on sapphire. For quartz and mica, as there is some overlap (indicated by the purple box in Figure 6.2C) in their particle numbers throughout the reactions, no comparisons were made regarding their nucleation rates.

To explore the possible mechanisms causing the fastest heterogeneous nucleation to occur on sapphire despite its positive charge, we recall classical nucleation theory (CNT). Based on CNT (details in Supporting Information),\textsuperscript{109} fast heterogeneous nucleation prefers a high local saturation ratio ($\Omega$), high substrate–solution interfacial energy ($\sigma_{sl}$), and low precipitate–substrate interfacial energy ($\sigma_{ps}$). The first parameter, the local saturation ($\Omega$), cannot be the dominant mechanism controlling the heterogeneous nucleation, as the local saturation index ($\Omega$) was expected to be the lowest on sapphire, as discussed in Section 4.2.

We then considered the substrate–solution interfacial energy ($\sigma_{sl}$). As discussed in Section 3.3, the order of the $\sigma_{sl}$ values was $\sigma_{\text{quartz–water}} < \sigma_{\text{mica–water}} < \sigma_{\text{sapphire–water}}$. A higher substrate–
solution interfacial energy ($\sigma_{sl}$) promotes heterogeneous nucleation; thus, the highest sapphire-water interfacial energy would have promoted the fastest heterogeneous nucleation on sapphire.

Finally, we considered the precipitate–substrate interfacial energy ($\sigma_{ps}$), which is related to the crystal structural mismatch between the substrate and the precipitates. A higher structural mismatch results in a higher $\sigma_{ps}$. Because the precipitates and the substrates belong to different crystal systems (Table 6-S1 in Supporting Information), we cannot calculate the exact lattice mismatch, but the metal–oxygen and oxygen–oxygen bond length mismatches can be compared as an alternative. As shown in Table 6-S2, among the three substrates, the bond length mismatch is the smallest between sapphire and the precipitates, i.e., the Fe–O (2.0 Å) and O–O (2.8 Å) bond lengths of Fe(III) (hydr)oxides are similar to the Al–O (1.9 Å) and O–O (2.7 Å) bond lengths of sapphire. The smallest crystal structural mismatch between sapphire and the precipitates should therefore result in the lowest precipitate–substrate interfacial energy for sapphire, promoting the fastest heterogeneous nucleation on sapphire compared to the other two substrates.

To sum up, our observations and analysis suggested that the interfacial energies ($\sigma_{sl}$ and $\sigma_{ps}$) within the liquid–substrate–precipitate system played a more crucial role in the heterogeneous nucleation process than the local saturations, which controlled the heterogeneous growth rates. Considering the importance of heterogeneous nucleation and the extremely limited data currently available for the interfacial energies of the liquid–substrate–precipitate system, further exploration of this area is an important future direction. To more accurately calculate the interfacial energies between the substrate surfaces and the precipitates, we could measure the in situ contact angles between the substrate surfaces and the precipitates, or study the
heterogeneous nucleation rates under different saturation indices. Further exploration on this area is our undergoing research and is beyond the scope of the current manuscript.

6.5. Environmental Implications

Using GISAXS, this study provides for the first time quantitative information about both the size and volume evolutions of Fe(III) (hydr)oxide particles precipitated on environmentally ubiquitous mineral surfaces. This technique allowed us to separately look into the heterogeneous nucleation and growth processes. Interestingly, both the fastest nucleation and slowest growth occurred on sapphire. Interfacial energies and local saturations were found to be the controlling mechanisms for heterogeneous nucleation and growth, respectively. New information on the heterogeneous nucleation and growth of Fe(III) (hydr)oxides provided in this study can be incorporated into reactive transport modeling. Although current reactive transport models have significantly improved our ability to predict the fate and transport of contaminants, there are still limitations in providing accurate data on the rates of heterogeneous nucleation and growth, and resulting changes in mineral surface area, and reactivity. Here we provided new quantitative information that can help predict contaminant transport in many aqueous environments, including the pollutant transport induced by CO₂ injection or leakage.

Acknowledgments

This work is supported by a Washington University Faculty Start-up Grant and the National Science Foundation’s Environmental Chemical Science Program (CHE-1214090). We thank Jessica Ray for HRTEM measurements and Dr. Soenke Seifert for beamline experimental help. Use of the Advanced Photon Source (Sector 11-BM and 12ID-B) at Argonne National
Laboratory was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.
Experimental Methods and Data Analysis Details

**Cleaning procedure for the single crystal substrates.** Quartz and mica sheets were purchased and cut to 1 cm × 1 cm pieces to fit into the GISAXS cell. To remove the surface contaminants, the quartz and mica pieces were sonicated in acetone for 10 minutes. Then, the quartz pieces were further soaked for 1 h in a highly concentrated sulfuric acid solution mixed with a commercial oxidizing agent, Nochromix®. Finally, all quartz and mica samples were rinsed with ultrapure water (resistivity >18.2 MΩ-cm) and stored in micro-filtered distilled water. For sapphire, 1 cm × 1 cm square sapphire samples with an atomically flat (0001) surface (C-plane) were purchased from MTI Corporation, CA. Each wafer had been packed in a 1000 class clean room using a 100 grade plastic bag with a wafer container. Right before GISAXS measurement, the package was opened and sapphire samples were rinsed with ultrapure water (resistivity >18.2 MΩ-cm).

**Solution preparation.** Solutions were prepared with reagent grade Fe(NO$_3$)$_3$•9H$_2$O, NaNO$_3$, and ultrapure water. Right before GISAXS or zeta potential measurements, ultrapure water was added to the weighed salt (0.0452 g NaNO$_3$) to a final solution volume of 45 ml and shaken to mix. Then, ultrapure water was added to 0.0202 g Fe(NO$_3$)$_3$•9H$_2$O to get a final solution volume of 50 ml, which we also quickly shook to mix. Finally, 5 ml of this 10$^{-3}$ M Fe(NO$_3$)$_3$ solution was
added into the 45 ml salt solution and the solution was shaken. The final 50 ml solution contained $10^{-4}$ M Fe(NO$_3$)$_3$ and had an ionic strength of 10 mM. Because hydrous Fe(III) oxide precipitation started when the $10^{-3}$ M Fe(NO$_3$)$_3$ solution was prepared, timing started from this mixing moment. Only approximately 2 min elapsed before the first GISAXS image was taken.

**Preparing quartz, mica, and sapphire powders in acidic salt solution for zeta potential measurements.** Quartz, mica, and sapphire were ground to powder, and each was separately allowed to settle in an acidic salt solution (10 mM NaNO$_3$, with pH around 3.7 ± 0.2, adjusted with HNO$_3$) for 10 min. Then, the upper region of each solution, which contained only small suspended quartz/mica/sapphire powder, was injected into a zeta cell for zeta potential measurements.

**Quartz, mica, and sapphire structures.** Quartz, mica, and sapphire crystal structures are shown in Figure 6-S1 using a polyhedral model. The red balls represent oxygen, and the polyhedrons are formed by straight lines connecting the centers of the anions which surround the cations. The polyhedron vertices touch one another at the centers of the anions, and the numbers of vertices of a polyhedron equal the coordination numbers of the cation inside the polyhedron.

The quartz structure can be described as a network of interconnected Si tetrahedra (Figures 6-S1A1 and 6-S1A2). The angle of the central O-Si-O inside the tetrahedral is 109.5°, while the angle of the Si-O-Si bond bridging these tetrahedra is 144°.

Muscovite (Figure 6-S1B1) has a plate-like structure consisting of two tetrahedral (T) Si/Al sheets connected by an Al dioctahedral (O) sheet, forming the so-called T-O-T structures. The tetrahedral Al/Si ratio is 1/3, and due to this isomorphous substitution of the tetravalent silicon by trivalent aluminum, there is an excess negative surface charge in the tetrahedral layer, which
is compensated by the interlayer cations, such as K\(^+\), shown as the purple balls in Figure 6-1B1.\(^{209}\) Cleavage along the (001) plane of muscovite exposes the tetrahedral layer, which is constructed by connected six-member rings, as shown in Figure 6-S1B2.\(^{209}\) The long-range distribution of Si and Al in the tetrahedral layers is disordered, while the short-range ordering follows the Loewenstein Al-avoidance rule.\(^{210}\)

For sapphire (\(\alpha\)-Al\(_2\)O\(_3\)), which contains Al\(^{3+}\) and O\(^{2-}\) ions, the crystal lattice takes the form of a slightly distorted closest hexagonal packing of O\(^{2-}\) anions, with the Al\(^{3+}\) cations filling two thirds of the octahedral hollows between the closely packed O\(^{2-}\) anions (Figures 6-S1C1 and S1C2).\(^{173}\) The coordination numbers for Al\(^{3+}\) and O\(^{2-}\) are 6 and 4, respectively.\(^{173}\)

**Nucleation rate.** According to classical nucleation theory (CNT)\(^{109}\), for mineral nucleation to occur, a free energy barrier (\(\Delta G^*\)) must be overcome. The energy barrier originates from the positive contribution of the interfacial free energy to the total free energy change associated with the creation of a crystal precipitate from solution. Taking the nucleation barrier as the activation energy for nucleation to occur, the nucleation rate (I), which is the increase in the number of nuclei per unit volume per unit time, can be described in eqn. S(1), where k is the rate constant:

\[
I = k \exp\left(-\frac{\Delta G^*}{RT}\right) \text{cm}^{-3} \text{sec}^{-1} \quad S(1)
\]

During homogeneous nucleation, a solution–precipitate interface is created, and the nucleation energy barrier, \(\Delta G_{\text{hom}}^*\), as shown in eqn. S(2) and S(3), is a function of the interfacial energy between the precipitates (\(p\)) and solution (\(l\)), \(\sigma_{pl}\), and the energy barrier for bulk crystal growth (\(\Delta G_l\)), which is a function of the saturation ratio of the solution (\(Q/K\)).\(^{109}\) According to
eqn. S(1), S(2) and S(3), a higher saturation ratio (Ω) and a lower \( \sigma_{pl} \), which results in a lower nucleation energy barrier, are preferred for faster homogeneous nucleation.

\[
\Delta G^*_{\text{homo}} = \frac{16 \pi \nu^2 \sigma^3_{pl}}{3 \Delta G^2_r} \tag{S(2)}
\]

\[
\Delta G_r = -RT \ln \Omega = -\ln 10 \times RT \times \log \Omega \tag{S(3)}
\]

where \( \nu \) is the molecular volume.

During heterogeneous nucleation, the interfacial free energy originates from the creation of the precipitate \((p)\)–substrate \((s)\) interface and the precipitate \((p)\)–solution \((l)\) interface, as well as the partial covering of the substrate \((s)\)–solution \((l)\) interface, as shown in eqn. S(4):

\[
\Delta G_{\text{interface}} = A_{pl} \sigma_{pl} + A_{ps} (\sigma_{pl} - \sigma_{sl}) \tag{S(4)}
\]

where \( A_{pl} \) and \( A_{ps} \) are the surface areas between the precipitate–liquid and precipitate–substrate interfaces.\(^{109}\) Considering both the interfacial energy (\( \Delta G_{\text{interface}} \)) and the energy barrier for bulk crystal growth (\( \Delta G_r \)), a higher saturation ratio (Ω) and substrate–solution interfacial energy (\( \sigma_{sl} \)), and a lower precipitate–substrate interfacial energy (\( \sigma_{ps} \)) are preferred for faster heterogeneous nucleation.

**GISAXS scattering curve fitting.** The 1D scattering curves (Figure 6.1) were fit to eqn. S(5), where \( P(q, R, \sigma) \) is the form factor, and \( S \) is the structure factor.

\[
I(q) = I_0 P_0(q, r_0, \sigma_0) S(q, i_0, \sigma_0, d, R_h, \nu_f) + I_1 P_1(q, r_1, \sigma_1) \tag{S(5)}
\]

\[
P(q, R, \sigma) = (\Delta \rho)^2 \int n(R, \sigma) V^2 \frac{9 (\sin (qR) - qR \cos (qR))^2}{(qR)^6} dR \tag{S(6)}
\]
\[ S(q, I_{os}, d, R_h, v_f) = I_{0s}q^d + S(q, R_h, v_f) \]  

For the form factor \( P(q, r, \sigma) \), a polydisperse sphere model with the Schultz distribution as a size distribution function was used, as shown in eqn. S(6). \( n(R, \sigma) \) is the Schultz distribution function used to represent the observed size polydispersity of the particles.\(^{139} \) \( \Delta \rho \) is the electron density difference between the nanoparticles and solutions, and \( V \) is the particle volume.

The particles showed interparticle distance peaks and power law behavior in the low q range, which can be modeled by the structure factor, \( S(q, I_{os}, d, R_h, v_f) \) as shown in eqn. S(7). The first term, \( I_{0s}q^d \), models the aggregates, where \( I_{0s} \) is a scaling constant and \( d \) is the Porod power-law exponent for the aggregates.\(^{211} \) The second term, \( S(q, R_h, v_f) \), models the local structure in the aggregates. We used the structure factor derived from the hard-sphere Percus-Yevick model, with \( R_h \) and \( v_f \) being the hard-sphere interaction distance and volume fraction, respectively.\(^{212} \)

**Particle size, volume, and number calculations.** The fitted values of \( R \) and \( \sigma \) after reaction for different times were used to calculate the evolution of the average radii of gyration (\( R_g \), Figure 6.2A) of the primary particles, according to the Schultz distribution function. Based on calculations, the sizes of the nanoparticles on the substrates grew from around 1–2 nm to 4–6 nm. Based on DLS measurements, the homogeneously precipitated particles in solution were around 10 nm, bigger than the observed particles on the substrates (4–6 nm). Thus, we confirmed that there was no significant deposition of the homogeneously precipitated particles from solution onto the substrates, and therefore, the particles on substrates were formed through heterogeneous nucleation and growth. Therefore, we can use the scattering signals from the nanoparticles on surfaces to study the heterogeneous nucleation and growth processes.
To calculate the relative total particle volumes (Figure 6.2B), the fitted intensities \( I \) were used for the integration to calculate the invariant 
\[
Q = \int_0^\infty I(q)q^2dq.
\]
In our previous work, \(^{168}\)Fe(III) precipitation experiments were conducted at the same aqueous condition in the presence of quartz. With 10 times higher X-ray intensity, we were able to observe the \( q \) range from 0.005 to 0.2 \( \text{Å}^{-1} \) with good signal to noise ratio, and we were able to observe the 1 nm particle (at \( q \) around 0.05-0.2 \( \text{Å}^{-1} \)) formation at later reaction time (after 40 min). In the current study, because of the much lower X-ray intensity, the signal to noise ratio was low at the high \( q \) range, thus, we were unable to resolve the 1 nm particle clearly. For simplicity, we focused only on the evolution of the initially 2 nm particles, and fittings were conducted over the \( q \) range of 0.005 to 0.08 \( \text{Å}^{-1} \). Also because of the noise data at high \( q \) range, the invariants were not calculated from the measured data. Considering the perfect agreement between the measured intensities and the fitted curves (Figure 6.1) over the fitting region, the invariants were calculated from the fitting curve, which can be extended to an infinite \( q \) range based on simulation. In this way, the calculated invariants represent the total volumes of the larger particles grown from 2 to 6 nm (\( V \), Figure 6.2B), and did not include the volume of the 1 nm particles.

Then, assuming a spherical particle shape and using the total particle volumes of the larger particles (\( V \), Figure 6.2B) and their average particle sizes (\( R_g \), Figure 6.2A), the total particle numbers (\( N \), Figure 6.2C) were calculated in relative units: 
\[
N = \frac{V}{R_g^3}.
\]
The particle sizes on sapphire were small (image A); therefore, according to the equation, a small fluctuation in the fitted particle sizes (\( R_g \)) will cause large fluctuation in particle numbers (\( N \)) on sapphire, as shown in Figure 6.2C. Even considering this fluctuation, we can conclude that the particle numbers on sapphire increased with time and were the most among the three substrates (as
shown by the guideline in Figure 6.2C).
Table 6-S1 Space groups and lattice parameters of iron (hydr)oxides, quartz, mica, and sapphire.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>5.0380</td>
<td>13.7720</td>
<td>R 3 (-)c</td>
</tr>
<tr>
<td>ferrihydrite</td>
<td>5.95</td>
<td>9.06</td>
<td>P63mc</td>
</tr>
<tr>
<td>goethite</td>
<td>a = 9.9134, b = 3.0128</td>
<td>c = 4.5800</td>
<td>P nma</td>
</tr>
<tr>
<td>lepidocrocite</td>
<td>a = 3.0800, b = 12.5000</td>
<td>c = 3.8700</td>
<td>Cmc2(1)</td>
</tr>
<tr>
<td>akaganeite</td>
<td>a = 10.587, b = 3.0311</td>
<td>c = 10.515, Z = 1; β = 90.03°</td>
<td>I2/m</td>
</tr>
<tr>
<td>sapphire</td>
<td>4.7540</td>
<td>12.9900</td>
<td>R3(-)c</td>
</tr>
<tr>
<td>quartz</td>
<td>4.9137</td>
<td>5.4047</td>
<td>P3(1) 2 1</td>
</tr>
<tr>
<td>muscovite</td>
<td>a = 5.1890, b = 8.9960</td>
<td>c = 20.0960, β=95.1800</td>
<td>C2/c</td>
</tr>
</tbody>
</table>
Table 6-S2 Average bond lengths of iron (hydr)oxides, quartz, mica, and sapphire.\textsuperscript{34, 207, 208}

<table>
<thead>
<tr>
<th>Material</th>
<th>O–O (Å)</th>
<th>Cation–O (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>ferrrihydrite</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>goethite</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>lepidocrocite</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>sapphire</td>
<td>2.7</td>
<td>1.9</td>
</tr>
<tr>
<td>quartz</td>
<td>2.6</td>
<td>1.6</td>
</tr>
<tr>
<td>muscovite</td>
<td>2.8</td>
<td>1.6 (Si-O), 1.9 (Al-O)</td>
</tr>
</tbody>
</table>
Figure 6-S1 Polyhedron models of crystal structures for quartz (A), muscovite (B), and sapphire (C). The plots were created using Crystal Maker (CrystalMaker® for Windows, version 2.5.2, CrystalMaker Software Ltd.).
Figure 6-S2 AFM observations of cleaned quartz (A), mica (B), and sapphire (C) surfaces before reactions. The height profiles provided below the images were cut along the dashed white lines.
Chapter 7. Conclusions and Future Directions

7.1 Conclusions

To ensure safe and efficient GCS operations, it is important to understand the fast geochemical reactions induced during CO\textsubscript{2} injection or its leakage, which can affect the porosity, permeability, and the transport of pollutants in aquifers. However, such reactions, especially at nanoscale and microscale, have been far from well-understood because of their complexity. At field sites, clay mobilization has been reported to decrease the aquifer’s permeability during water flooding. Also, Fe dissolution and its later precipitation and adsorption of pollutants has been observed at GCS field sites. Motivated by these field site observations, the present work chose to investigate CO\textsubscript{2}–brine–mica interactions under relevant GCS conditions and to study Fe(III) (hydr)oxide precipitation at nano- and micro-scale.

Tasks 1 and 2 determined CO\textsubscript{2}–brine–mica interactions under varied acidic hydrothermal conditions relevant to different GCS sites. Tasks 3 and 4 quantitatively analyzed the homogeneous and heterogeneous nucleation and growth kinetics of Fe(III) (hydr)oxide at brine (water)–rock interfaces.

In Task 1, biotite dissolution and the consequential morphological changes and secondary mineral phase precipitation were investigated under relevant GCS conditions (102 atm CO\textsubscript{2} pressure and 95°C, in 1 M NaCl solution). Al-substituted goethite and kaolinite were the main precipitates observed on the biotite edge surfaces. On biotite basal plane, macroscopic fibrous illite precipitation on flat surface and their later detachment from the cracked biotite basal
surface were observed. Fibrous illite growth in sandstone reservoirs has been reported to severely decrease the porosity and permeability of the reservoir, resulting in serious problems for hydrocarbon production.\textsuperscript{36} We also observed a fast ion exchange reaction with aqueous Na\(^+\) and biotite interlayer K\(^+\), which was thought to have caused the biotite swelling and cracking, as well as promoting the fast fibrous illite precipitation.

In Task 2, the effects of aqueous composition, temperature, and CO\(_2\) pressure on biotite alteration were investigated. Faster ion exchange reactions (Na\(^+\)–K\(^+\), Mg\(^{2+}\)–K\(^+\), and Ca\(^{2+}\)–K\(^+\)) occurred in the salt solutions than in water (H\(^+\)–K\(^+\)). The ion exchange reactions affected the formation of swelling-related morphologies (bump, bulge, and crack) on the biotite basal plane, as well as the release of biotite framework ions. In these salt solutions, numerous illite fibers precipitated after reaction for only 3 h at 95°C. Interestingly, oriented aggregation of illite nanoparticles forming the fibrous-shaped illite was observed during slow illite precipitation in water, as well as in salt solutions at lower temperatures. This observation suggested oriented aggregation as a new mechanism for fibrous illite formation, different from the traditional mechanisms of preferred growth over a certain direction. Based on Si release over the temperature range of 35-95°C, the activation energy of biotite dissolution was calculated to be 52 ± 5 kJ mol\(^{-1}\). By comparison with N\(_2\) experiments, CO\(_2\) injection was observed to greatly enhance biotite’s dissolution and its surface morphology evolutions, such as crack formation and detachment of newly formed fibrous illite. Besides the pH effect, aqueous CO\(_2\) can also promote mica cracking, probably through intercalation into the mica interlayer.

In Task 3, SAXS/GISAXS experiments were conducted to quantify in situ the size and volume evolutions of the Fe(III) (hydr)oxide nanoparticles in solution (homogeneously precipitated) and on quartz (heterogeneously precipitated) in the presence of ubiquitous anions.
(NO$_3^-$, Cl$^-$, and SO$_4^{2-}$). For all three systems, particles in solution were bigger than the particles on quartz. Compared with NO$_3^-$, the volume of Fe(III) (hydr)oxide precipitates was much less in Cl$^-$ system, especially for the heterogeneous process. The inhibition was caused by the complexation of Cl$^-$ with the Fe(III) (hydr)oxide, which hindered the polymerization of Fe(III) (hydr)oxide. In the SO$_4^{2-}$ system, the neutralization of the charge of the Fe(III) (hydr)oxide precipitates caused their fast growth on quartz and fast aggregation in solution.

In **Task 4**, the *in situ* size and volume evolutions of the Fe(III) (hydr)oxide nanoparticles on quartz, mica, and sapphire were quantified. Then, the total particle numbers and the growth rates of particle sizes were calculated, which represent the heterogeneous nucleation and growth kinetics of Fe(III) (hydr)oxides, respectively. Based on the calculations, both the fastest nucleation and slowest growth occurred on sapphire. Water contact angles and zeta potentials were measured. Electrostatic forces between the charged Fe(III) (hydr)oxide prenucleation clusters (PNCs) and substrate surfaces—which affect local saturations near the substrate surfaces—controlled heterogeneous growth rates. Water contact angles indicated a highest substrate-water interfacial energy for sapphire. Further, comparison of structural mismatches between the substrates and precipitates indicated a lowest precipitate-substrate interfacial energy for sapphire. The fastest nucleation on sapphire suggested that interfacial energies in the solution–substrate–precipitate system controlled the heterogeneous nucleation rates.

### 7.2 Recommended Future Directions

In our study, numerous fibrous illite precipitates were observed on biotite after reaction under hydrothermal conditions for only 3 h. Fibrous illite has been reported to affect reservoir permeability more significantly than platy illite, and it could cause serious challenges to oil
production. Thus, a better understanding of the shapes and formation kinetics of illite is crucial for predicting the fate and transport of reservoir fluid and permeability changes in subsurface environments, and it would be an important future direction to study the effect of environmental factors (such as temperature, organics, and substrates) on illite’s formation kinetics and shapes. It could also be interesting to conduct flow-through experiments with mica-containing caprock and CO\textsubscript{2} saturated brine, to directly measure the porosity and permeability changes caused by the formation and mobilization of fibrous illite.

Also, we observed that aqueous CO\textsubscript{2} can promote mica cracking, and hypothesized that CO\textsubscript{2} intercalation was a potential mechanism. At GCS sites, caprock could interact with aqueous CO\textsubscript{2} dissolved in brine. However, so far, no direct experimental measurements have been conducted for the potential mica swelling caused by aqueous CO\textsubscript{2} interaction. Considering the importance of the interaction of clay with CO\textsubscript{2} molecules in brine at GCS sites, experimental observations or molecular simulations of the intercalation of aqueous CO\textsubscript{2} into clay interlayers can be important future directions.

Finally, based on our observations and analysis of the heterogeneous nucleation and growth of Fe(III) (hydr)oxide on different mineral surfaces, we found that the interfacial energies (\(\sigma_{sl}\) and \(\sigma_{ps}\)) within the liquid–substrate–precipitate system played an essential role in the heterogeneous nucleation process. Considering the importance of heterogeneous nucleation and the extremely limited data currently available for the interfacial energies of the liquid–substrate–precipitate system, further exploration of this area is an important future direction. To more accurately calculate the interfacial energies between the substrate surfaces and the precipitates, we could measure the \textit{in situ} contact angles between the substrate surfaces and the precipitates.\textsuperscript{42}
study the heterogeneous nucleation rates under different saturation indices, or compare the critical nuclei sizes and nucleation rates on different substrates.

In summary, inspired by GCS field site observations, we studied the fast nano- and micro-scale geochemical reactions, including CO₂-brine-mica interactions and Fe(III) (hydr)oxide precipitation, that affect the porosity, permeability, and pollutant transport in aquifers. New qualitative and quantitative information as well as scientific insights were provided, which can guide safer and more efficient operation of many subsurface projects, including but not limited to geologic CO₂ sequestration. Future directions were also suggested, which can promote further discovery and investigation of this topic.

Yandi Hu helped with the aquatic chemistry analysis and conducting the GISAXS experiments
Appendix A. *In situ* Determination of Interfacial Energies between Heterogeneously Nucleated CaCO$_3$ and Quartz Substrates: Thermodynamics of CO$_2$ Mineral Trapping

Results of this chapter have been published in Environmental Science & Technology, 2013, 47 (1), 102-109.

Abstract

The precipitation of carbonate minerals—mineral trapping—is considered one of the safest sequestration mechanisms ensuring long-term geologic storage of CO$_2$. However, little is known about the thermodynamic factors controlling the extent of heterogeneous nucleation at mineral surfaces exposed to the fluids in porous reservoirs. The goal of this study is to determine the thermodynamic factors controlling heterogeneous nucleation of carbonate minerals on pristine quartz (100) surfaces, which are assumed representative of sandstone reservoirs. To probe CaCO$_3$ nucleation on quartz (100) in solution and with nanoscale resolution, an *in situ* grazing incidence small angle X-ray scattering technique has been utilized. With this method, a value of $\alpha' = 36 \pm 5$ mJ/m$^2$ for the effective interfacial free energy governing heterogeneous nucleation of CaCO$_3$ has been obtained by measuring nucleation rates at different solution supersaturations. This value is lower than the interfacial energy governing calcite homogeneous nucleation ($\alpha \approx 120$ mJ/m$^2$), suggesting that heterogeneous nucleation of calcium carbonate is
favored on quartz (100) at ambient pressure and temperature conditions, with nucleation barriers between 2.5% and 15% lower than those expected for homogeneous nucleation. These observations yield important quantitative parameters readily usable in reactive transport models of nucleation at the reservoir scale.

A.1. Introduction

Carbon capture and sequestration in deep geologic reservoirs such as depleted oil and gas fields, coal beds, or saline aquifers is considered to be one of the main options to mitigate the current increasing CO₂ emissions over the next century.¹ Within geologic CO₂ sequestration (GCS), stable carbonate mineral formation—mineral trapping—is one of the sequestration mechanisms that will assure long-term storage of CO₂.²,³ The precipitation of carbonate minerals is a widely studied chemical process due to the widespread formation of these minerals in marine and sedimentary environments,⁴,⁵ and because of its importance in many industrial processes which include the production of construction materials, ceramics, fillers, absorbents or the inhibition of scale formation.⁶ However, the extreme physico-chemical conditions present in the subsurface reservoirs targeted as potential hosts for the CO₂ make prediction of the mineralization processes difficult, especially as these are expected to occur over long time spans relative to laboratory experiments.⁷

A combination of thermodynamic and kinetic factors contributes to this uncertainty. Low supersaturations for carbonate phases are expected in GCS sites due to the relatively low solution pH values, which will be driven down upon injection of supercritical CO₂ (scCO₂) by formation of carbonic acid. Additionally, slow dissolution kinetics of silicate minerals, which are expected
to be the main sources for cations, has been commonly hypothesized to be the limiting step for carbonation reactions.\textsuperscript{8,9} These slow kinetics are affected by the formation of mineral coatings (\textit{e.g.} amorphous silica), which in some cases act as passivating agents of the silicate mineral surface, inhibiting further dissolution.\textsuperscript{9–11} Interestingly, some studies have pointed out that, under certain conditions, the slow precipitation kinetics of carbonate minerals can be the limiting step for the carbonation reaction.\textsuperscript{12,13} For instance, Saldi et al. reported magnesite precipitation rates two to three orders of magnitude slower than forsterite dissolution rates\textsuperscript{12}. Giammar et al. showed that Mg- and Si-rich carbonated solutions supersaturated with respect to magnesite can maintain the supersaturation, making the nucleation of magnesite the limiting-step for the carbonation reaction.\textsuperscript{13} In addition, the same authors observed that magnesite seeds present in the solutions accelerated the precipitation.\textsuperscript{13} The presence of a mineral surface is expected to lower the free energy barrier for heterogeneous nucleation if the interfacial free energy of the substrate–crystal interface is lower than that of the liquid–substrate interface.\textsuperscript{14} In view of these results, and considering the ubiquity of mineral surfaces that could promote mineral formation in porous reservoirs, it becomes important to quantify the thermodynamic drivers for heterogeneous nucleation in order to accurately assess the extent of nucleation processes in subsurface environments.

The influence of quartz as a seed material for CaCO\textsubscript{3} precipitation has been studied previously by different authors. Lin and Singer used titration experiments at relatively high salinities (0.1 M KCl), and observed no catalytic effect.\textsuperscript{15} The same result was obtained by Kralj and Vdovic, who also used high salinity solutions (0.5 M NaCl).\textsuperscript{16} A more recent study by Lioliou et al.\textsuperscript{17} reported two different results: On one side, the presence of quartz does not influence the measured induction time with respect to the one observed for pure CaCO\textsubscript{3} saturated
solutions. This suggests that heterogeneous nucleation is not taking place, and therefore it concludes that quartz does not provide a favorable surface for heterogeneous CaCO$_3$ nucleation, at least under relatively high salinity conditions. On the other hand, in another experiment in which quartz grains were added to highly saturated CaCO$_3$ solutions, these authors observed an increase of the precipitation rate. Using fits to a polynuclear growth model, the authors obtained a value for the interfacial free energy of the water–CaCO$_3$–quartz system equal to 31.1 mJ/m$^2$. It is worth noting that the technique used by these authors does not specifically look at the size evolution of the precipitates, but at the changes in the chemistry of the bulk fluid, and is probably unable to detect the early stages of the nucleation. In this sense, our experimental approach provides unique information by using an *in situ* technique that allows probing the size and the relative change of the total number of CaCO$_3$ particles nucleated under different supersaturation conditions at the nanometer scale.

Of all potential carbonate minerals, Ca$^{2+}$, Fe$^{2+}$, and Mg$^{2+}$ carbonates are the most likely mineral phases to control carbonate concentrations in subsurface environments, due to the release of these cations upon dissolution of the silicate minerals in typical reservoir lithologies.$^3$ As a first step, and due to the kinetic limitations governing Mg$^{2+}$ and Fe$^{2+}$ carbonate formation, we have chosen to work with CaCO$_3$.$^{18}$ Also, we have performed our experiments at ambient pressure and room temperature and circum-neutral solution pH. Although these conditions are different from the high pressures and temperatures present in geologic CO$_2$ reservoirs, our study will provide new fundamental thermodynamic information about the nucleation processes that will still be valid under real reservoir conditions, such as the value for the interfacial free energy between the quartz substrate and the nucleated crystals. Due to the inverse solubility of carbonate minerals, the high temperature will be an additional driving force for nucleation, but it is not
expected to influence the value for this interfacial free energy. Also, given the fact that the point of zero charge for the surface of quartz (100) is at pH\textsubscript{PZC} = 2.8\textsuperscript{19} and that significant surface charge does not develop on quartz until pH exceeds 8\textsuperscript{19}, we expect that the surface charge of quartz under the conditions of our experiment will be very similar to the one expected at the lower pH ranges expected in geologic reservoirs, which have typical pH values of ~3.1 upon injection of scCO\textsubscript{2} and pH values between 5.5 to 6.7 after mineral dissolution has taken place\textsuperscript{20}.

The goal of the present study was two-fold: (a) to develop an in situ GISAXS technique that allows determining interfacial free energies between nucleating particles and mineral substrates in an open system (i.e., keeping a constant flow of solution over the surface), and (b) to apply this technique to the study of the water–CaCO\textsubscript{3}–quartz system. Our unique in situ experimental approach allowed us gaining important fundamental information about the thermodynamics of heterogeneous nucleation, and it opens the possibility for studying the influence that solution ionic strength, interface surface roughness and heterogeneity, and other physico-chemical parameters can exert over nucleation processes in subsurface environments.

A.2. Experimental Section

In situ time-resolved GISAXS setup. The experimental setup used in this study was optimized from a similar setup developed in our group previously for in situ GISAXS batch experiments\textsuperscript{21,22}. Mineral substrates were placed horizontally in a flow-cell designed ad hoc for the nucleation experiments. The cell internal dimensions are 10 mm × 10 mm × 15 mm. Two Kapton windows allow an X-ray beam to be directed to the substrate with an incidence angle \( \alpha_i = 0.14^\circ \), lower than the critical angle for total reflection (\( \alpha_{c-quartz} \approx 0.16^\circ \) at 12 KeV incident X-ray energy), so that the X-ray beam is reflected by the substrate. CaCl\textsubscript{2} and NaHCO\textsubscript{3} solutions
were flowed from two reservoirs of 1L each using two peristaltic pumps (model WPX1-F1/8S4-C, Welco Co. Ltd., Tokyo, Japan) at a rate of 1.6 mL/min, and mixed in a home-made mixing cell equipped with a rotating stir bar just before the solution was injected to the flow-cell. The residence time of the fluid in the cell was minimized in previous tests with colored dyes, and was estimated to be $\tau_{\text{res}} \approx 10$ seconds. This time is lower than the acquisition time of GISAXS images, ensuring that the fluid supersaturation, and thus the thermodynamic driving force for nucleation, was kept constant throughout the duration of the experiment. The scattered intensity from the nucleated CaCO$_3$ particles was collected using a 2-dimensional Pilatus 2M detector (Dectris Ltd., Baden, Switzerland) available at the beamline 12ID-B at the Advanced Photon Source (Argonne National Laboratory, USA). An incident radiation of 12 KeV X-ray energy and a sample-to-detector distance of $d_{\text{s-d}} = 2215$ mm, allowed covering a $q$-range of $0.005 \, \AA^{-1} < q < 0.3 \, \AA^{-1}$.

**Substrate and solution preparation.** Quartz (100) substrates (MTI Corp., CA, USA) were rinsed with acetone, ethanol, isopropanol, and de-ionized water (all chemicals were ACS reagent grade, from Sigma Aldrich), and subsequently cleaned using a mixture of Nochromix (Godax Labs Inc, MD, USA) and sulfuric acid for 2h to eliminate any organics from the substrates. They were stored in de-ionized water and dried with N$_2$ prior to the X-ray scattering experiments. The roughness of the substrates was measured using an Atomic Force Microscopy apparatus prior to the experiments, yielding $R_q$ values $R_{q-\text{quartz}} \approx 1$ nm. CaCl$_2$ and NaHCO$_3$ solutions of different concentrations (see Table 1A) were prepared at the APS prior to the start of the scattering experiments. The pH of the mixed solution was monitored prior to the start of every experiment, and the supersaturation calculated using the speciation code Phreeqc Interactive (version 2.17.5, 2010)$^{23}$ and the Minteq database. Saturation index with respect to amorphous calcium carbonate has been calculated using the solubility constant reported by Brecevic and Nielsen (1989).$^{24}$
Scattering data processing and analysis. Images of the scattered intensity were acquired every 2 minutes, with a lapse time of 10 seconds between images. Dark current subtraction and transmission normalization were applied to all the images before data analysis. The transmission was calculated from the values of the incident and the transmitted intensity as measured using an ionization chamber and a photodiode placed on the beam stop, respectively. To isolate the scattering signal from the nucleated particles from any parasite interface scattering, the first image acquired after the substrate is completely covered by the solution has been subtracted from the rest. The scattering intensity for an isotropic system is proportional to:

\[ I_{GISAXS}(q) = I(0) \times P(q,R,\sigma_d) \times S(q) \]  \hspace{1cm} (1)

where \( P(q,R,\sigma_d) \) is the form factor, \( S(q) \) is the structure factor and \( q \) is the momentum transfer. The average vertical and lateral particle sizes can be obtained from the distribution of the scattering intensity along the momentum transfer directions perpendicular (\( q_z \)) and parallel (\( q_{xy} \)) to the plane of the substrate, respectively. To this end, the 2-dimensional images were integrated using vertical and horizontal cuts of the intensity. The intensity in the extracted 1-dimensional curves was modeled using a log-normal polydisperse model of non-interacting spherical particles, with:

\[ P(q,R,\sigma) = (\Delta \rho)^2 \int n(R,\sigma_d) V^2 \frac{9(\sin(qr) - qR \cos(qR))^2}{(qR)^6} dR \]  \hspace{1cm} (2)

where \( n(R,\sigma_d) \) is the log-normal distribution, which is used to represent the observed size polydispersity of the nucleated particles, with \( R \) being the mean radius of the particle and \( \sigma_d \) its standard deviation. \( V \) and \( \Delta \rho \) are the particle volume and the electronic density difference (or contrast) between the particle and the surrounding solution. The IRENA package was used to
perform fits of the experimental data.\textsuperscript{27} The use of a spherical model for the particle shape is based upon the observation of isotropic scattering in the 2-dimensional images. Non-spherical shapes would yield different distributions of the scattering radiation.\textsuperscript{25}

**Classical nucleation theory.** Two main parameters control the height of the thermodynamic barrier for nucleation of a new phase from a saturated solution: the interfacial free energy, $\alpha'$, and the supersaturation, $\sigma$.\textsuperscript{14} The supersaturation is defined as: $\sigma = \ln[(Ca^{2+})(CO_{3}^{2-})/K_{sp}]$, where the terms in the parenthesis denote the activity of Ca\textsuperscript{2+} and CO\textsubscript{3}\textsuperscript{2-} respectively. The nucleation rate, $J_n$, can be expressed as:

$$J_n = A \exp\left(-\frac{\Delta g_n}{k_BT}\right) = A \exp\left(-\frac{16\pi v_m^2 \alpha'^3}{3k_B^2 T^3 \sigma^2}\right) \tag{3}$$

where $\Delta g_n$ is the free energy change associated with the nucleation of the new phase, $v_m$ is the molar volume of the nucleated phase divided by the Avogadro number, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $A$ is a kinetic factor containing another exponential law and an activation energy related to the kinetic pathways involved in nucleation. Homogeneous nucleation processes are governed by interfacial free energies between the nucleated particles and the solution ($\alpha' = \alpha_{lc}$). In the case of heterogeneous nucleation processes, three different interfacial free energies come into play: the liquid–nucleating crystal interfacial free energy $\alpha_{lc}$, the liquid–substrate interfacial free energy $\alpha_{ls}$ and the substrate–crystal interfacial free energy $\alpha_{cs}$. A fourth parameter, the contact angle $\theta$ between the nucleated particle and the substrate, is also an independent variable in the definition of the effective interfacial free energy for a spherical cap particle $\alpha'$ (see equation S2 in the Supporting Information). Assuming a hemi-spherical particle ($\theta = 90^\circ$), equation S2 reduces to:\textsuperscript{28}
\[ \alpha' = \frac{\alpha_{sc}}{2^{1/3}\left(1 - \frac{\alpha_{b} - \alpha_{sc}}{2\alpha_{tc}}\right)} \] (4)

A complete characterization of the thermodynamics of heterogeneous nucleation is thus possible if the nucleation rate is determined experimentally, and the other parameters in equations (3) and (4) are known. The GISAXS experiments described here have been designed to obtain the rate of heterogeneous nucleation of CaCO\textsubscript{3} on quartz from the fits of a simple polydisperse model of spherical particles to the data. Experiments have been performed in a flow-through system to keep \( \sigma \) constant. Nucleation rates at different \( \sigma \) values have been obtained by making use of the SAXS invariant, \( Q \).\textsuperscript{26}

\[ Q = (1/2\pi^2) \int q^2 I(q) dq \] (5)

A.3. Results and Discussion

Horizontal cuts to the normalized scattering data from one representative time-resolved experiment are shown in Figure A.1. A power law behavior is observed at early stages of the nucleation experiment, with no particle scattering visible. With time, an increase in the scattered intensity is observed at intermediate \( q \) values. This is associated with the formation of CaCO\textsubscript{3} particles on the quartz substrate. A fit to the data in this region using a spherical model and a log-normal distribution to represent the polydispersity yields a mean particle size (radius) of \(~2\) nm (see Supporting Information), with typical standard deviation values of \(~0.09\) nm. At longer times (\(~54\) minutes for the example shown in Figure A.1), a different process is observed, with the intensity from the particle scattering decreasing at the same time as the exponent of the power law behavior observed at low \( q \) is decreased from \(-2.9\) to \(~0\). This trend, which has been
observed in all the experiments, can be interpreted based on previous studies as a change in the aggregation state of particulates formed by the ~2 nm elementary particles.\textsuperscript{29,30} The apparent formation of a peak at around $q = 0.03$ Å\(^{-1}\) at long times (Figure A.1b, 140 min) indicates that inter-particle correlations between the elementary CaCO\(_3\) particles are present, which could be modeled using an inter-particle structure factor.\textsuperscript{29,31,32} It is worth noting that all the curves also show power law behavior at very low $q$ that could be associated with larger size entities. We hypothesize that the observed aggregation process is the basis of an aggregation-based growth model in which large crystals with sizes not probed within the $q$-range of these experiments are formed with time. Confirmation of the existence of these larger crystals is given by the observation that at long times ($t > 100$ min for the experiment shown in Figure A.1) the scattered intensity around the beam center increases and shows reflections typical of faceted crystalline particles (see Figure A-S2 in the Supporting Information). A more complex analysis using different levels of mass fractal aggregate models could have been applied if the data quality would have been better. The curve at 54 min in Figure A.1A could be decomposed into two different linear regions with different mass fractal exponents, indicating that the aggregate structure could have several levels of complexity.\textsuperscript{32,33} However, the low statistics of our data sets—due to the low contrast between the nucleated particle and the surrounding solution and to the thick beam path through water (1 cm)—prevent any complex analysis of the data. Thus, we have restricted our data analysis to the time points during which the intensity is increasing (time points from 0 to 54 mins in Figure A.1A). In the data analysis we have interpreted the scattered curves using the simplest approach, with a single particle scattering region at medium and high $q$ range plus a power law to describe the intensity at low $q$. No attempt has been made to model the structure factor observed in the curves at long times. More experiments at lower $q$ ranges are
needed to understand the size evolution of the aggregates, which is beyond the scope of this manuscript.

**Figure A.1.** Horizontal cuts of the GISAXS intensity corresponding to experiment S3 (see Table 1A). (A) Particle scattering with an extended Guinier region is observed to develop with time. A fit to the data gives a very polydisperse population of particles with average particle size of ~2 nm. (B) After a given time, the slope of the particle scattering starts to decrease, concomitantly with a decrease of the negative slope of the signal at low $q$ associated with a change in the aggregation state of the ~2 nm particles. The gaps in the data are due to a gap between different panels in the 2-dimensional detector.

Analyzing the development of particle scattering at the initial stages of the experiments (such as those presented in Figure A.1A) under different supersaturation conditions allows us to obtain thermodynamic information of the CaCO$_3$–quartz system. The observed increase of the intensity at early stages of the experiment is associated with the formation of ~2 nm primary particles. Interestingly, the size of these primary particles remains constant during these initial stages (see fits of the data at different time points in the Supporting Information). According to equations (1) and (2), three factors affect the total level of scattered intensity, namely the contrast ($\Delta\rho$), the square of the particle volume ($V$) and the number of particles ($n$). The fact that no
change is observed in the size of the particles during these initial stages of the experiments, and under the assumption that the nature of the CaCO$_3$ polymorph that is being formed remains unchanged, we can make the assumption that $V$ and $\Delta \rho$ are constant. The increase in the intensity can thus be solely ascribed to the nucleation of primary particles. The X-ray scattering invariant represents the integrated scattering intensity and is proportional to the total volume of particles irradiated by X-rays multiplied by the mean square of the electron density differences between the particles and water.$^{26}$

**Figure A.2.** (A) Fits to the data at two different time points corresponding to experiment S3. The Lorentz-corrected SAXS scattering function is plotted (thick dashed lines). The invariant $Q$, proportional to the total mass nucleated, is equivalent to the area subtended underneath the thick dashed lines. (B) Evolution of the invariant with time at different supersaturations, and linear fits to the data.

Plots of the so-called Lorentz-corrected GISAXS intensity ($f(q) = I(q) \cdot q^2$) for two representative curves from the same experiment shown in Figure A.1 are shown in Figure A.2A. These curves have been calculated from the fitted function to the experimental data, which allows extrapolating the data at high $q$ values and obtaining a converged value for the invariant at each time point. The invariant is equivalent to the subtended area underneath the Lorentz-
corrected GISAXS intensity curves. Plots with the time-evolution of the invariant for a set of experiments at different solution supersaturation values are shown in Figure A.2B, together with linear fits to the data. Following the observation that the size of the primary particles is constant throughout the early stages of the experiment, the slope of each of these curves is then equivalent to the rate of heterogeneous nucleation of CaCO$_3$ on quartz. The resulting nucleation rates are presented in Table 1A, and their natural logarithm plotted against $1/\sigma^2$ in Figure A.3. A linear regression of this plot yields a value for the slope that can be interpreted in terms of an interfacial free energy $\alpha'$ by using equation (3). From this, the value of the crystal–substrate interfacial free energy $\alpha_{cs}$ can be obtained using equation (4). However, some further hypotheses are required to make the calculations: (a) In order to obtain a value for the interfacial free energy $\alpha'$ the nucleated polymorph should be identified, so that the correct value for the molar volume ($v_m$) can be used in equation (3). Unfortunately, no information about the nature of the polymorph is available from the GISAXS experiment. In the absence of the information needed to ascertain the nature of the ~2 nm nucleated particles, we decided to interpret the result by making two different assumptions about the nature of the polymorph, assuming the molar volumes for calcite$^{34}$ and for amorphous calcium carbonate (ACC) (see Supporting Information). (b) Also, values for the interfacial free energies between the water and the nucleated crystals are needed ($\alpha_{lc}$). To our knowledge this value has only been reported for the surface of calcite (10-4), showing a large variability: values of $\alpha_{\text{water-calcite}}$ range from 83 to 170 mJ/m$^2$.$^{35-38}$ In view of this variability, we decided to adopt a mean value of $\alpha_{\text{water-calcite}} = 120$ mJ/m$^2$. For ACC, $\alpha_{\text{water-ACC}}$ is not known. However, given the highly hydrated state of ACC, we can make the reasonable assumption that this value must be lower than the minimum value that has been reported for calcite. Therefore, the value of $\alpha_{\text{water-ACC}}$ was assumed to be 50 mJ/m$^2$. Our choice of calcite and
ACC as the possible nucleating polymorphs is founded also on the fact that their $\alpha_{lc}$ values are probably placed at the ends of the range of values expected for aragonite and vaterite (whose $\alpha_{lc}$ values are unknown). The same holds for the values of $v_m$, with the exception of aragonite, that is denser than calcite. However, aragonite is rarely observed as the first polymorph nucleated (in the absence of Mg$^{2+}$), being ACC and vaterite the typically observed polymorphs in Ostwald ripening processes. It is also worth noting that, based the ACC solubility constant reported by Brecevic and Nielsen, ACC is not expected to nucleate under the conditions used in our experiments. However, the current on-going debate in the literature about the possibility that CaCO$_3$ pre-nucleation clusters—formed in undersaturated conditions with respect to calcite—act as precursors for the nucleation of other polymorphs has prompted us to consider the possibility that ACC is the nucleating phase.\textsuperscript{39,40} (c) The third parameter of relevance is related to the shape of the nucleated particles. This is important because the contact angle of the nuclei with the substrate has an influence on the exact form of equation (S4).\textsuperscript{14,41} However, the small size of the nucleated particles observed in the GISAXS experiments lead us to question whether it is reasonable to define a shape for these small molecular clusters. For the sake of simplicity, and in the absence of further experimental evidence (\textit{e.g.}, high resolution microscopy data at the early stages of nucleation), a hemi-spherical shape ($\theta = 90^\circ$) has been assumed (results using other $\theta$ values are presented in the Supporting Information). (d) Values for the liquid-substrate interfacial free energies $\alpha_{ls}$ are needed if equation (4) is to be solved completely. Surprisingly, there are few reports for these values in the literature, and they are quite different from each other. Parks\textsuperscript{42} reported a value $\alpha_{\text{water-quartz}} = 360 \pm 30$ mJ/m$^2$, which differs greatly from the $\alpha_{\text{water-quartz}} = 120$ mJ/m$^2$ reported by Rimstidt and Cole\textsuperscript{43} and is smaller than the value $\alpha_{\text{water-quartz}} = 416$ mJ/m$^2$ published by Iler.\textsuperscript{44} In a subsequent study, Mizele et al.\textsuperscript{45} reported a value for the water–
amorphous silica interface of $\alpha_{\text{water-am-silica}} = 340 \text{ mJ/m}^2$, which compares well with the value for quartz reported by Parks.$^{42}$ Amorphous silica and quartz surfaces differ on the different proportions of silanol groups on their surface and on the higher presence of defects present on the surface of amorphous silica, which might tend to increase the value of the liquid–substrate interfacial free energy.$^{45}$ However, a large variation in the value of $\alpha_{ls}$ is not expected.$^{42,45}$ According to this, we used the $\alpha_{\text{water-quartz}} = 360 \pm 30 \text{ mJ/m}^2$ value reported by Parks,$^{40}$ which agrees well with the Mizele et al.$^{43}$ and is an intermediate value between all the reported values for the water–quartz interface.

![Figure A.3. Plots of the measured nucleation rates against the inverse of the squared supersaturation. The obtained slope is proportional to the effective interfacial free energy $\alpha'$. The data from two different synchrotron runs are shown.](image)

211
The values for the different interfacial free energies calculated following the aforementioned assumptions are presented in Table 1B. If calcite is assumed to be the nucleated polymorph, a value of $\alpha' = 36 \text{ mJ/m}^2$ is obtained. Instead, if the ~2 nm particles are assumed to be ACC nanoparticles, the interfacial free energy governing heterogeneous nucleation is decreased to a value of $\alpha' = 27 \text{ mJ/m}^2$. These two values compare well with a previously measured value of $\alpha' = 31.1 \text{ mJ/m}^2$ reported by Lioliou et al. using a similar plot of the CaCO$_3$ precipitation rate (measured using bulk concentrations of CaCO$_3$) versus the inverse of the supersaturation. However, these authors used a powder of quartz grains that was added to a supersaturated CaCO$_3$ solution after homogeneous nucleation had been initiated. It is thus possible that the agreement between both $\alpha'$ values is purely coincidental. In this sense, the fact that we are probing heterogeneous nucleation directly at the water-mineral interface, using a nanoscale in situ technique, and averaging over a large area of the substrate (the fingerprint of the X-ray beam on the substrate is about 1000 mm$^2$) makes our approach unique.

The fact that both $\alpha'$ values are smaller than $\alpha_{\text{water-calcite}} = 120 \text{ mJ/m}^2$ implies that the thermodynamic driving force for heterogeneous nucleation of CaCO$_3$ on quartz is higher than for homogenous nucleation. A comparison between the height of the molar free energy barriers for nucleation ($\Delta g_n$) for both processes gives a ratio $\Delta g_{n-het}/\Delta g_{n-homo} \times 100 = 2.5\%$ for calcite and an estimated ratio of $\Delta g_{n-het}/\Delta g_{n-homo} \times 100 = 15\%$ lower if ACC is the nucleated polymorph. This implies that, if nucleation is an activated process, heterogeneous nucleation will be more significant over homogeneous nucleation, given that kinetically-limiting factors for both processes are unimportant. An interesting point worth underlining here is that heterogeneous nucleation processes dominate even though obtained interfacial free energies $\alpha_{\text{calcite/ACC-quartz}}$ have relatively high values if compared, for instance, with values of $\alpha_{\text{water-calcite/ACC}}$. The effect of the
substrate is represented in equation (4) by the factor in the parenthesis. If this factor is equal to 1, the interfacial free energy governing the nucleation barrier would be equal to $\alpha_{lc}$, which would be the case for a process of homogeneous nucleation. If the term in the parenthesis is larger than 1, then heterogeneous nucleation is not favored thermodynamically and homogeneous nucleation will dominate. For heterogeneous nucleation to be favorable from a thermodynamic point of view, the term in the parenthesis has to be lower than 1. This condition is fulfilled as long as the interfacial free energy between the solution and the substrate is larger than the interfacial free energy between the nucleated crystal and the substrate ($\alpha_{ls} > \alpha_{cs}$). This can be interpreted as a ‘competition’ between the solution and the nucleating crystal for the substrate. Substrate hydrophilicity/hydrophobicity (associated with $\alpha_{ls}$) and lattice mismatch (associated with $\alpha_{cs}$) are thus the key parameters controlling heterogeneous nucleation.

**Environmental implications for geologic carbon sequestration.** The results presented here suggest that quartz is a favorable substrate for the nucleation of CaCO$_3$ under ambient conditions of pressure and temperature. This is a factor that can be readily included in pore scale reactive transport models of CaCO$_3$ nucleation where mineralogy is dominated by quartz, such as sandstone reservoirs. If the value for the interfacial energy obtained remains unchanged at the high temperatures and pressures present in geologic CO$_2$ storage reservoirs, and given that the nucleation process is not governed by kinetic factors, this could have significant implications in the prediction of sandstone reservoir permeability/porosity relationships, which are dependent on the spatial distribution of the precipitates.$^{46}$ Of course, conditions in geologic reservoirs will be different, with temperature and pressures typically higher than those of the critical point for CO$_2$ (31.1 °C and 7.38 MPa).$^{47,48}$ High temperature will be an additional driver for nucleation given the inverse solubility of carbonate minerals. However, the effect of both high pressure and
temperature over the relative driving forces for heterogeneous \(i.e.,\) interfacial free energies) and homogeneous nucleation has not yet been obtained.

It is well known that the wettability of mineral surfaces decreases after being in contact with scCO\(_2\), becoming thus more hydrophobic.\(^{49-51}\) According to the previous discussion, this change will affect the thermodynamics of nucleation by changing the difference between the term \(\alpha_{ls}\), which will increase (this term is minimum in the case of an ideal water/water interface), and the term \(\alpha_{cs}\), whose evolution is uncertain. The magnitude of \(\alpha_{cs}\) is mostly controlled by the lattice mismatch between substrate and the nucleating crystal at the interface.\(^{52}\) Given that the change in wettability will be mostly due to changes in the hydroxylation state of the substrate, as suggested by Chiquet et al.,\(^{50}\) or to the capping of silanol groups with CO\(_2\), as suggested by Dickson et al.,\(^{51}\) and assuming no change in the lattice mismatch, one could hypothesize that the change in \(\alpha_{cs}\) will be small. Under this assumption, the contact with scCO\(_2\) is expected to increase the thermodynamic driving force for heterogeneous nucleation by providing an increase of \(\alpha_{ls}\) that would lower the effective interfacial free energy for nucleation, \(\alpha'\). One interesting point is that the sole examination of \(\alpha_{cs}\) cannot provide enough information of the likelihood of heterogeneous nucleation processes, which would be favored as long as \(\alpha_{cs}\) is lower than \(\alpha_{ls}\). This fact highlights the need for an accurate determination of liquid–substrate interfacial free energies. The lack of this information not only affects our ability to predict accurately thermodynamic controls on nucleation processes, but it also prevents us from determining accurately the thermodynamics factors controlling dissolution processes. As reported by Lasaga and Blum\(^{53}\), the critical free-energy \(\Delta G_c\) for the formation of an edge pit in a mineral surface depends directly on the value of the liquid–substrate interfacial free energy. This fact emphasizes the urgent need for more research in this direction.
Another important finding provided by a close examination of equation (4) is the fact that high salinity causes an increase of $\alpha_{ls}$, as has been shown by Mizele et al.$^{45}$ in amorphous silica surfaces in contact with a 1 M NaCl solution. This is of special relevance for mineral carbonation in reservoir rocks due to the fact that some of the targeted sedimentary reservoirs are connected with salt domes, which requires that the pore-space water have high salinities up to 2 M NaCl.$^{20,54,55}$ A similar effect could be observed in depleted oil reservoirs proposed as potential CO$_2$ sequestration sites. The elevated concentrations of hydrophobic organic molecules forming coatings of mineral surfaces could increase the value of $\alpha_{ls}$, as indicated by Butkus and Grasso$^{56}$ in organic-water interfaces. Salinity and organic coatings could therefore act as potential drivers for enhanced heterogeneous nucleation, from a purely thermodynamic point of view. Further investigations are needed to ascertain the effects that high ionic strength or the presence of organic molecules might have on the nucleation kinetics of metal carbonates.

**Acknowledgements**

We gratefully acknowledge James J. DeYoreo for numerous discussions and for his insightful comments and suggestions, as well as the constructive comments from four reviewers. Also, Jessica Ray (WUSTL), Xiaobing Zuo, Janae DeBartolo and Sonke Seifert (APS, ANL) are thanked for their help during GISAXS data collection. A.F.-M. thanks Giuseppe Saldi, Damien Daval and the ‘Amorphous Reading Group’ for enjoyable discussions about this and other subjects over the last two years. This material is based upon work supported as part of the Center for Nanoscale Control of Geologic CO$_2$, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-AC02-05CH11231. Use of the Advanced Photon Source, an Office of Science User Facility
operated for the U.S. Department of Energy Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.
Supporting Information for Appendix A

Contents: Experimental details

One table (A-S1)

Five figures (A-S1 – A-S5)

Determination of the molar volume of amorphous calcium carbonate

The density of amorphous calcium carbonate (ACC), and thus its molar volume, was determined by using the X-ray absorption spectroscopy method reported by Shen et al. (2002)\(^1\). Briefly, a ~100 \(\mu\)m diameter hole of a Rhenium gasket is completely filled up with ACC. The gasket is loaded in a Diamond Anvil Cell and the absorption of ~20 KeV X-rays through the sample is measured using two ionization chambers placed on both sides of the sample along the X-ray beam path. Making use of the relationship between density and absorption coefficient,\(^1\) the density of the sample can be measured. A value of \(\rho = 2.19 \text{ g/cm}^3\) for ACC was found using this method.

Interfacial free energies error analysis

The errors reported together with the values of the interfacial free energy correspond to twice the standard error obtained from the fit of the nucleation rates over \(1/\sigma^2\), as shown in Figure A.3 in the main text of the manuscript. The errors plotted in Figure A.3 correspond to twice the standard error obtained from the fits of the curves in Figure A.2B. The robustness of our experimental approach is shown in Figure A.3, where results from two different synchrotron runs are presented showing almost identical values for the interfacial free energy.

Homogeneous, heterogeneous and secondary nucleation
The possible contribution from homogeneous nucleation of CaCO$_3$ was tested by performing an experiment in which transmission SAXS images were taken through the solution (~ 1 cm above the quartz surface) after every GISAXS image was collected, with the same acquisition time of $t_{\text{acq}} = 1$ minute for each image. The integrated intensities (horizontal cuts for the GISAXS images, and 360$^\circ$ circular integration for the SAXS images) are shown in Figure A-S1. It can be observed that, while the SAXS intensity remains constant, particle scattering is developed in the GISAXS image over time, with values of the maximum intensity at least 1 order of magnitude larger than the SAXS intensity.

The possibility of secondary nucleation has been discarded by the fact that the size of the formed particles remains constant during the initial stages of nucleation probed in these experiments. For secondary nucleation to occur, a large CaCO$_3$ particle that would act as substrate should have been present in the solution. If this was true, the scattered intensity should show a change in the slope at a lower Q value than the observed one. Because this is not observed in our experiments, we conclude that the effect of secondary nucleation, if any, is negligible.

**Examples of fits to experimental data for other $\sigma$ values**

Representative examples of experimental data covering long time spans are shown in Figure A-S4 together with the fit to the data using a log-normal polydisperse spherical model. The resulting mean radius ($R$) and standard deviation ($\sigma_d$) for the data shown are presented in Table S1. The probability density function of the log-normal distribution is defined as:

$$p(r; R, \sigma_d) = \frac{1}{r \sigma_d \sqrt{2\pi}} e^{-\frac{(\ln r - R)^2}{2\sigma_d^2}}$$  \hspace{1cm} (S1)
where \( R \) is the mean particle size, \( \sigma_d \) is the standard deviation and \( r \) is the independent variable.

**Substrate – nucleated particle interfacial free energy \( \alpha_{sc} \) as a function of the contact angle \( \theta \)**

The linear regression of the nucleation rates measured as a function of solution supersaturation values (see Figure A.3 in the manuscript) has been interpreted in the main text of the manuscript by adopting a hemispherical model for the nucleated particles (\( \theta = 90^\circ \)). However, if a spherical particle with an arbitrary contact angle \( (0^\circ \leq \theta \leq 180^\circ) \) is assumed, the value for the interfacial free energy \( \alpha_{sc} \) varies as indicated in Figure A-S5, according to the following expression (equation (4) in the main text of the manuscript):

\[
\alpha' = \alpha_{lc} \frac{2(1 - \cos \theta) - \sin^2 \theta \frac{\alpha_{ls} - \alpha_{sc}}{\alpha_{lc}}}{2^{2/3} (2 - 3 \cos \theta + \cos^3 \theta)^{2/3}} \tag{S2}
\]

As it can be seen in Figure A-S5, the \( \alpha_{sc} \) values obtained assuming both ACC and calcite as the nucleating polymorphs vary from maximum values \(~255 \text{ mJ/m}^2\) and \(~335 \text{ mJ/m}^2\) respectively to non-physical negative values at very large contact angles. Even though more information about the molecular-scale mechanistic process of the critical nuclei formation is needed to make sense of these values, some discussion can be made about the obtained values. Interestingly, the values for ACC in the region from \( 0^\circ \) to \(~100^\circ\) fall within a window of values of \( \pm 10 \text{ mJ/m}^2\). This range is shorter from calcite (values of \(~255 \pm 10 \text{ mJ/m}^2\) from \( 0^\circ \) to \( 60^\circ \)). This suggests that, if ACC is the nucleating polymorph, then the contact angle \( \theta \) could have a much larger variability than in calcite, without affecting the value of \( \alpha_{sc} \). This implies that if the value of \( \alpha_{sc} \) is imposed by a certain nucleation mechanism, the formation of ACC would have more ‘flexibility’ than the formation of calcite in terms of contact angle with the substrate.
Figure A-S1. Plot of the GISAXS and SAXS intensities in an experiment with $\sigma_{\text{calcite}} = 3.78$.

The SAXS intensity remains constant and at least one order of magnitude lower than the GISAXS intensity.
The observation of sharp reflections (lines) indicates the formation of crystal faces on the precipitate. The fact that the lines originate from the beam center is indicative of large particles (out of the experimental q-range probed by our experiment).
**Figure A-S3.** The experimental setup for the GISAXS experiments is shown in the picture. (1) In situ flow through cell. The substrate is placed in horizontal. (2) Vacuum tube bringing the incident X-ray beam to the sample. (3) Vacuum tube though which the scattered X-rays are directed to the detector (far at the left in the image). (4) Peristaltic pumps used to pump the CaCl$_2$ and NaHCO$_3$ solutions to the mixing cell. (5) Mixing cell where the two solutions are mixed before being injected to the cell.
Figure A-S4. Representative experimental data points covering wide range of time spans. The fits to the data using a polydisperse spherical model are shown.
Figure A-S5. Values of the substrate – nucleated crystal interfacial free energy obtained as a function of the contact angle, using equation (S2). The values of $\alpha_{lc}$ and $\alpha_{ls}$ have been fixed to the values shown in Table 1B ($\alpha_{ls} = 360$ mJ/m$^2$; $\alpha_{lc}$-calcite = 120 mJ/m$^2$; $\alpha_{lc}$-ACC = 50 mJ/m$^2$). The yellow region highlights the region where negative (non-physical) values for $\alpha_{sc}$ are found.
**Table A-S1.** Fitted values of the mean particle radius ($R$) and its standard deviation ($\sigma_d$) for different samples covering a wide range of time points.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{\text{calcite}}$</th>
<th>Time (min)</th>
<th>$R$ (nm)</th>
<th>$\sigma_d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>3.98</td>
<td>6</td>
<td>2.5</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>2.51</td>
<td>0.086</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>2.51</td>
<td>0.085</td>
</tr>
<tr>
<td>S2</td>
<td>3.78</td>
<td>15</td>
<td>1.5</td>
<td>0.089</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>1.51</td>
<td>0.088</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37</td>
<td>1.42</td>
<td>0.091</td>
</tr>
<tr>
<td>S3</td>
<td>3.31</td>
<td>15</td>
<td>3.21</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>3.20</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27</td>
<td>3.1</td>
<td>0.59</td>
</tr>
<tr>
<td>S4</td>
<td>2.76</td>
<td>79</td>
<td>3.0</td>
<td>0.089</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99</td>
<td>3.1</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td></td>
<td>199</td>
<td>2.98</td>
<td>0.080</td>
</tr>
<tr>
<td>S5</td>
<td>2.16</td>
<td>100</td>
<td>2.4</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td></td>
<td>170</td>
<td>25.7</td>
<td>0.065</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>2.8</td>
<td>0.063</td>
</tr>
</tbody>
</table>

Yandi Hu contributed to the the CO$_2$ exposure experiments of Shewanella oneidensis MR-1 and their viability analysis.
Appendix B. Viability and Metal Reduction
of Shewanella Oneidensis MR-1 under CO\textsubscript{2}
Stress: Implications for Ecological Effects of
CO\textsubscript{2} Leakage from Geologic CO\textsubscript{2}
Sequestration

Results of this chapter have been published in Environmental Science & Technology, 2010, 44 (23), 9213–9218.

Abstract

To study potential ecological impacts of CO\textsubscript{2} leakage to shallow groundwater and soil/sediments from geologic CO\textsubscript{2} sequestration (GCS) sites, this work investigated the viability and metal reduction of Shewanella oneidensis MR-1 under CO\textsubscript{2} stress. While MR-1 could grow under high-pressure nitrogen gas (500 psi), the mix of 1% CO\textsubscript{2} with N\textsubscript{2} at total pressures of 15 or 150 psi significantly suppressed the growth of MR-1, compared to the N\textsubscript{2} control. When CO\textsubscript{2} partial pressures were over 15 psi, the growth of MR-1 stopped. The reduced bacterial viability was consistent with the pH decrease and cellular membrane damage under high pressure CO\textsubscript{2}. After exposure to 150 psi CO\textsubscript{2} for 5 h, no viable cells survived, the cellular contents were released, and microscopy images confirmed significant cell structure deformation. However, after a relatively short exposure (25 min) to 150 psi CO\textsubscript{2}, MR-1 could fully recover their growth within 24 h after the stress was removed, and the reduction of MnO\textsubscript{2} by MR-1 was observed right after the stress was removed. Furthermore, MR-1 survived better if the cells were
aggregated rather than suspended, or if pH buffering minerals, such as calcite, were present. To predict the cell viability under different CO₂ pressures and exposure times, a two-parameter mathematical model was developed.

### B.1. Introduction

The amount of carbon dioxide (CO₂) from anthropogenic emissions has dramatically increased in the past several decades, which raises global climate-change concerns. CO₂ sequestration in deep geological formations (i.e., geologic CO₂ sequestration, GCS), such as deep saline aquifers, provides a promising option for us to significantly reduce net CO₂ emissions to the atmosphere within a relatively short period (Figure B.1)²¹³-²¹⁵. For successful geologic CO₂ sequestration, the injected CO₂ should remain stable in the GCS sites. However, zero leakage of CO₂ from GCS projects may not be possible. Analog studies of geologic environments containing large, concentrated amounts of CO₂ have shown that the leakage processes is inherent in GCS²¹⁶. Leaking of CO₂ could be due to the presence of preexisting geological discontinuities, the weakening of the caprock caused by interactions with CO₂, or incidental breakouts through injection wells, existing wells, or seismic disturbances²¹³. It has been estimated that allowing for no more than 1% leakage of stored CO₂ over 100 years is necessary for sequestration to be viable²¹⁷. Once any leakage from deep geological formations occurs, CO₂ can migrate through overlying potable aquifers and induce geological, chemical, and/or microbiological changes in shallow groundwater, which can be an underground source of drinking water (USDW), and in soil/sediment environments (Figure B.1)²¹³,²¹⁵,²¹⁸-²²⁰. Dissolved in groundwater, CO₂ increases the total concentration of aqueous carbonate species, including \( \text{H}_2\text{CO}_3 \), \( \text{HCO}_3^- \), and \( \text{CO}_3^{2-} \), and causes a decrease in pH. Such conditions can also influence the
viability and activity of microorganisms, while changing the reaction mechanisms of dissolution, adsorption, precipitation, and redox reactions occurring on mineral surfaces or in the aqueous phase. Systematic studies of potential impacts of CO₂ leakage on biogeochemistry and ecosystems are required to ensure safer GCS.

**Figure B.1.** Schematic diagram of potential scenario for ecological and environmental impact of CO₂ leakage from geologic CO₂ sequestration sires.

*Shewanella* species are environmentally relevant bacteria, widely existing in soil and sediments, where CO₂ leaking from sequestration sites may pass through (Figure B.1). *S. oneidensis* MR-1 is a model *Shewanella* strain and can grow in both aerobic and anaerobic environments (convenient for laboratory handling) due to its facultative anaerobic characteristics. In this study, *S. oneidensis* MR-1 is selected as a model microorganism in studying the effect of CO₂ leakage on the subsurface ecological system. In particular, the metal reducing capability of *S. oneidensis* MR-1 such as Fe(III), Mn(IV), and Cr(VI) in soil/sediment environments, is
an important aspect which can affect toxic metal mobility in the environment. Therefore, by examining S. oneidensis MR-1 physiology, the following crucial information can be obtained: (1) aerobic and anaerobic microorganism survival and recovery in response to various CO₂ conditions, and (2) the impacts of higher CO₂ concentrations owing to potential leakage on intrinsic microbial activities (i.e., metal reduction) and water chemistry changes in groundwater above GCS sites. Currently, a few studies have focused on utilizing biofilms to prevent CO₂ migration to upper geological matrices \(^{227,228}\), or on enhancing mineral-trapping and solubility-trapping though microbial ureolysis \(^{229}\). These approaches decrease the porosity and permeability of the caprock, potentially alleviating CO₂ leakage. However, little is known about the ecological impacts near GCS sites of exposure to high pressure CO₂.

To understand the influence of CO₂ leakage on microbial activity, we measured the changes in viability and metal reduction rates of MR-1 after exposure to increased CO₂ concentrations. Reduction rates of MnO₂ were used to evaluate the activity of MR-1 for three reasons: first, MnO₂ is widely distributed in the natural environment \(^{230}\). Second, it is one of the primary electron acceptors for organic matter oxidation and plays an important role in carbon mineralization in sedimentary environments \(^{223}\). Third, MnO₂ reduction by MR-1 is a relatively fast reaction \(^{222,223,226}\), which allows us to evaluate the activity of stressed MR-1 before it is recovered. We also examined bacterial responses to CO₂ stress in the presence of calcite coupons by combining biological and physico-chemical approaches. A mathematical model was built to quantitatively demonstrate and predict CO₂ stress on microbial survival in the ecological system. This study can help us understand the potential ecological effects of high-pressure CO₂ and provide guidelines to control CO₂ leakage from the GCS sites.
B.2. Materials and Methods

B.2.1. Reactor setup and experimental conditions

In this work, a bioreactor (Parr company, USA) was used to mimic the exposure of bacteria in groundwater to CO₂ leakage from GCS sites. This reactor was combined with a syringe pump connected to a CO₂ cylinder (99.9%, Airgas, USA) as a source for pressurized CO₂ (For more detailed information, refer to (Figure B-S1) and ref 17). Before the experiments, the reactor was flushed with CO₂ and/or N₂ (in some experiments) for two minutes to remove the air in the reactor. After that, the reactor was pressurized to the designated pressure through the syringe pump and pump controller. In this reactor setup, a temperature controller system maintained the reactor at a constant temperature (32 ± 0.5°C). CO₂ and N₂, singly and in mixtures, were used at a variety of pressures: 1% CO₂/99% N₂ (0.15 psi CO₂ in a total of 15 psi), 1% CO₂/99% N₂ (1.5 psi CO₂ in a total of 150 psi), 100% CO₂ (15 psi), 100% CO₂ (80 psi), and 100% CO₂ (150 psi). This tested CO₂ range covered the concentrations typically present either in flue gas from a conventional power station 231 or in groundwater 220.

B.2.2. Microorganism cultivation

*Shewanella oneidensis* MR-1 was first grown in a Luria-Bertani (LB) medium at 32 ± 0.5°C. The bacteria were then sub-cultured into an MR-1 medium (30 mM lactate as the carbon source) 226. When MR-1 growth reached the middle log phase (optical density (OD) measured at 600 nm was about 0.7), a second sub-culture (5% inoculation rate) was transferred into a modified MR-1 medium which supported anaerobic growth. The modified medium was supplemented with 40 mM fumarate (Sigma, USA) as an electron acceptor, and with 0.5 mM serine and 0.5 mM glycine (Sigma, USA) as nutrients to enhance cell growth 226. Falcon test
tubes with 4 ml of the cell culture (initial OD$_{600}$ ~ 0.2) were placed in the reactor for CO$_2$ exposure experiments. Control samples (without CO$_2$ stress) were cultured in sealed bottles (i.e., in a micro-aerobic condition). All culture experiments with CO$_2$ (including control samples) were kept at 32 ± 0.5 °C without shaking.

For CO$_2$ stress experiments, the cultures with or without calcite coupons were exposed to high pressure CO$_2$ in the reactor for a designated time. We added calcite coupons (0.12 g/ml; Iceland spar from New Mexico) to test the response of bacteria to CO$_2$ stress in the presence of pH buffering minerals. After CO$_2$ exposure, the total number of viable cells was estimated based on the number of colony-forming unit (CFU) after incubation at 32 ± 0.5 °C for 1-2 days. Averaged values and errors (standard deviations) of multiple samples (biological repeat, n ≥ 4) are presented in the Figures. The statistical significance of the mean values was examined by one-way analysis of variance at p < 0.05. To observe bacterial growth recovery after exposure to CO$_2$, the stressed cells (1 mL) were transferred into a tube filled with 5 mL of MR-1 minimal media and cultured in the incubator under aerobic conditions at 32 ± 0.5 °C. To examine the MR-1 cell aggregates under CO$_2$ stress, the cultures were filtered through a membrane (~1 cm × 1 cm, 0.22 µm pore size, Nylon, Millipore, USA) to form loosely-attached cell layers (cell density was ~8.0 × 10$^{10}$ cells/m$^2$) and then were transferred to the reactor for stress experiments.

B.2.3. Measurement of extracellular polymeric substances (EPS) and membrane integrity

In this study, the concentrations of EPS, including DNA, polysaccharides, and proteins, were analyzed. For EPS concentration, a modified EPS extraction method was utilized to quantify the EPS during experiments. The concentrations of polysaccharides and proteins
were analyzed according to methods described by Dubois et al. \textsuperscript{233} and Bradford \textsuperscript{234}, respectively. The integrity of the cytoplasmic membrane of cells was determined using a BacLight Live/Dead Kit (Molecular Probes, Invitrogen, USA). More detailed experimental descriptions are available in Supporting Information. For all the measurements, three biological repeats and two technical repeats were conducted.

**B.2.4. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) observations of microbial cells**

For SEM sample preparation, the cells were deposited on a piece of membrane, and then were fixed by adding 2\% glutaraldehyde. After 2 h, the samples were washed three times in 0.10 M sodium cacodylate buffer for 20 min each time. The samples were then dehydrated in series of 10 minute washes in 50\%, 70\%, 85\% and 95\% ethanol and were further dried with freeze-drier equipment (Labconco, USA). This procedure allowed us to maintain the cell morphology during SEM measurements \textsuperscript{235}. The samples were gold-coated using a sputter gun (SPI supplies, USA). Photographs of the sample structure were observed and taken with a SEM (FEI, UK).

For AFM observation of cells, the cells were deposited on a quartz coupon (~1 cm × 1 cm) in the presence of aqueous media. The heights, deflection, and friction images of the samples were collected simultaneously in contact mode using a Nanoscope V Multimode SPM (Veeco Instruments Inc., USA). Due to the strong stickiness of the released cell materials, the AFM observations were mainly focused on the cell morphology rather than the observation of released cell materials. Probes were made of non-conductive silicon nitride, with a tip height of 196 µm (NP-S10, Veecoprobes, USA). The images were collected with normal spring constants of 0.12
N/m and scan rates of around 1.5 Hz. Topographical features were analyzed using Nanoscope software (Version 7.20, Veeco Instruments Inc., USA).

**B.2.5. Measurements of Ca\(^{2+}\) release from calcite coupons, lactate consumption**

Cell cultures (OD\(_{600}\) ~0.25, viable cells ~10\(^8\)/ml) were added to two sterile bottles (20 ml). The same number of freshly cleaved calcite coupons was added in the same liquid/solid ratio as in all experiments conducted in the reactor. Both bottles were tightly covered with Parafilm\textsuperscript{®} laboratory film, and 100% CO\(_2\) (15 psi) was introduced from a CO\(_2\) cylinder (Airgas, USA) through pipelines to the headspaces of the bottles. The pH changes were monitored using a pH meter (Orion, Thermo Scientific, USA). Samples were collected at designated times (1, 5, and 17 h) with syringes, and were used to measure CFU and the concentrations of calcium ions (Ca\(^{2+}\)) and lactate. The calcium was measured with an inductively coupled plasma mass spectrometer (ICP-MS, Agilent, USA). Because lactate was the main carbon source for MR-1 growth, the consumption of lactate during the high CO\(_2\) stress conditions was also determined by a lactate assay kit (R-Biopharm, Germany).\textsuperscript{226}

**B.2.6. MnO\(_2\) reduction capability measurements**

Manganese reduction by stressed and unstressed cells was measured. The cells were exposed to 100% CO\(_2\) under 150 psi and 300 psi in the reactor at 32 ± 0.5°C (stressed cells) or were cultured in an incubator at 32 ± 0.5°C (non-stressed cells). Under the both conditions, fumarate was not added into the medium because it can compete with MnO\(_2\) for electrons. After 25 min, 30 mL of stressed or non-stressed cell cultures was placed in serum bottles and deoxygenated by sparging with nitrogen (atmosphere pressure) for 15 min (to achieve anaerobic
conditions). Then 1 g MnO$_2$ (Sigma-Aldrich, purity > 99%) was added to each serum bottle and nitrogen sparging was continued for another 3 minutes before the serum bottles were crimp sealed with Teflon-lined stoppers and aluminum seals. Then the bottles were placed on a rotating shaker (40 rotations per min) in an incubator at 32 ± 0.5°C in the dark (time $t_0$). At the desired time points, an aliquot of the suspension (including both the well-mixed liquid and solid) was withdrawn through the septum with a N$_2$ purged gastight syringe. Part of the suspension was used for CFU analysis, and the remainder was passed though a 0.22 μm filter and diluted with 2% HNO$_3$ solution for manganese measurement with ICP-MS. The reaction rates of MnO$_2$ were calculated from the data within the first 40 min by linear regression ($R^2 > 0.98$).

**B.3. Results and Discussion**

**B.3.1 Cell viability under CO$_2$ stress**

The growth and viability of MR-1 were strongly affected by both CO$_2$ partial pressure and exposure time. Figure B.2 shows the viable cells after MR-1 was exposed to CO$_2$ under partial pressures ranging from 0.15 to 150 psi. Under low CO$_2$ partial pressures (i.e., 0.15 and 1.5 psi, equivalent to 1% CO$_2$ when the pressures were 15 and 150 psi, respectively), the cell growth appeared to be inhibited. When the CO$_2$ pressure approached 15 psi (100% CO$_2$), the cell growth was completely stopped, and the viable cell numbers decreased as a function of exposure time. Increasing CO$_2$ pressure to 80 and 150 psi (100% CO$_2$) resulted in a dramatic drop of viable cells within 1 h, and no viable cells were detected after 5 h. For the experiment conducted at 150 psi (100% CO$_2$) for 1h, the OD values were also measured. The results showed that the OD values remained constant before or after CO$_2$ exposure while the CFU value decreased by
approximately two orders of magnitude. This suggests that only a small portion of cells remain viable, and the majority of cells were damaged or died.

\[ C/C_0 \]

**Figure B.2.** The measured growth and modeled growth of *S. oneidensis* MR-1 under CO\(_2\) stress (n ≥ 4). (◊) 1% CO\(_2\) (15 psi); (■) 1% CO\(_2\) (150 psi); (□) 100% CO\(_2\) (15 psi); (●) 100% CO\(_2\) (80 psi); (○) 100% CO\(_2\) (150 psi). The error bars are smaller than the symbols, and here unseen. The lines are the predicted curves based on fitting the data to Eq (2) and Eq (3). (Long dash) 1% CO\(_2\) (15 psi); (Dash) 1% CO\(_2\) (150 psi); (Square dot) 100% CO\(_2\) (15 psi); (Round dot) 100% CO\(_2\) (80 psi); (Solid) 100% CO\(_2\) (150 psi).

CO\(_2\) gas may affect microbial activity through three routes: high pressure stress on cellular structures, altered environmental pH from CO\(_2\) dissolution, and CO\(_2\) penetration intracellularly to interfere with metabolic functions. N\(_2\) gas was employed to study the effect of
pressure alone on bacterial viability. At N\textsubscript{2} gas pressures of 500 psi, bacterial growth was only slightly suppressed by about $13.0 \pm 0.5\%$ during a 17 h period (data not shown). Also, an experiment with a sudden influx of 100\% CO\textsubscript{2} at 150 psi, followed by its immediate release (within 5 sec, \textit{in situ} pH changed merely about 0.01 (Figure B-S2)) did not lead to any obvious influence on bacterial viability (similar CFU counts were detected; data not shown). Both phenomena indicate that pressure itself appeared not to be the key influence on microbial viability. Further, we examined pH conditions during CO\textsubscript{2} stress (atmosphere pressure). When 1.5 psi CO\textsubscript{2} was introduced into the bioreactor, the \textit{in situ} pH in the medium was 6.16 after 1 h exposure (Figure B-S2), and the viable cells were maintained at $59.1 \pm 7.4\%$ of the initial subcultures. In comparison, a culture with pH = 6.16 (adjusted by 0.2 M HCl, without CO\textsubscript{2} stress) did not result in any obvious changes in bacterial viability within 1 h (viable cells were kept at $100.0 \pm 8.6\%$). At 150 psi CO\textsubscript{2} for 1 h, the pH in the culture dropped to 4.86, and the viable cell amounts were about $0.7 \pm 0.1\%$. However, the culture with the same pH (pH only adjusted by HCl) without CO\textsubscript{2} stress had a cellular viability of $23.2 \pm 14.7\%$.

The above results indicate that besides the pH effect, CO\textsubscript{2} put significant stresses on cells. High pressure CO\textsubscript{2} can diffuse through cell membranes and dissolve intracellularly because of the hydrophobic and liposoluble properties of the cellular membrane. This process may increase membrane permeability, destroy the integrity of the cellular structure, and change the intracellular metabolic balance\textsuperscript{236-238}. This explanation was supported by the following observations: after exposure of cells to CO\textsubscript{2} (100\%, 150 psi) for 1 h, a significant amount of extracellular protein ($619 \pm 31$ mg/g of dry biomass) was released, whereas for unstressed cells, the value was only $282 \pm 14$ mg/g. The increase in extracellular protein for stressed cells was accompanied by an increase of free DNA concentration in the solution, from $17.8 \pm 0.3$ ng/µl for
unstressed cells to 27.4 ± 2.2 ng/µl. Furthermore, a decrease of membrane integrity index from 2.05 ± 0.18 for unstressed cells to 0.39 ± 0.06 for stressed cells was observed (Table S1).

**Figure B.3.** SEM and AFM images of *S. oneidensis* cells before and after CO₂ stress (100% CO₂, 150 psi). (A) and (D) Unstressed cells; (B) and (E) Cells after CO₂ stress for 30 min; (C) and (F) Cells after CO₂ stress for 5 h. (A), (B), and (C) are SEM images and (D), (E), and (F) are AFM images. The AFM micrograph is shown in height mode (15 × 15 µm²) at 298 K in air in the presence of aqueous media on quartz coupon surfaces. The height cross sections correspond to the white dotted lines in the AFM images.

SEM images (Figures B.3-A, B and C) show the morphological changes of cells with progressively longer CO₂ exposure times. AFM images (Figures B.3-D, E, and F) also indicate

238
that the unstressed cell thickness was 207 ± 42 nm, with a cell length ranging around 2.02 ± 0.32 μm (Figure B.3-D, profile-i). After exposure to CO₂ (150 psi) for 30 min and 5 h, respectively, the thicknesses of the cells were reduced to 102 ± 32 nm (Figure B.3-E, profile-ii) and 49 ± 11 nm (Figure B.3-F, profile-iii), respectively. The cell lengths were reduced to 1.60 ± 0.28 μm and 1.72 ± 0.32 μm (the values above are based on the measurement for 20 cells, and the uncertainties are standard deviations). These results confirmed that a large number of cells were collapsed, and thus cellular contents (such as protein and nucleotides) were released.

B.3.2 Alleviation of CO₂ stress under environmental conditions

Previous studies have reported that bacterial aggregates and biofilms could be considered as cellular response mechanisms to tolerate high CO₂ stress. In this study, loosely-attached microbial cell aggregates were developed by directly filtrating cells on a membrane (yielding a cell density of ~8.0x10¹⁰ cells/m²) and then exposing them to 100% CO₂ at 150 psi for 30 min. More viable cells (by 1~2 orders of magnitude) were achieved for aggregated cells than in the suspended culture (Table S1). This observation was consistent with findings in the literature that microbial cell aggregation can limit mass transport and create a micro-environment for cells to resist environmental stresses (such as pH and oxygen stress). Furthermore, when the stressed cells (100% CO₂ at 150 psi for 25 min) were transferred into a normal culture medium, their growth rate (defined by the change of OD values in an hour of bacterial growth) in the exponential phase was about 0.08 h⁻¹, which was clearly lower than that of unstressed cells (with a growth rate of 0.32 h⁻¹) (Figure B-S3B). However, the stressed cells could recover to the same cell density as the unstressed cells within 24 h after a long lag phase, which indicates that MR-1 displayed excellent recovery ability once the CO₂ stresses are removed.
Figure B.4. Changes of (A) CFU, (B) in situ pH values, (C) calcium concentrations and (D) lactate concentrations in the presence of calcite coupons under CO₂ stress (100% CO₂, 15 psi) (n ≥ 3). (○) Control cells; (□) Cells in the presence of calcite coupons. The error bars are smaller than the symbols, and here unseen.

The effect of calcite coupons on alleviating CO₂ stress to the cells was tested because calcite can serve as a pH buffering mineral in the presence of high pressure CO₂. Figure B.4A shows threefold viable cells were achieved after adding calcite coupons, compared to the number without calcite coupons. This finding corresponds to the fact that adding calcite coupons into the medium could lead to an increase of in situ pH by about 0.3 unit, after an equilibration process.
for 3 h (Figure B.4B). Figure B.4C suggests that calcite coupons gradually released \( \text{Ca}^{2+} \) in the solution (this concentration of \( \text{Ca}^{2+} \) could not directly inhibit the growth of MR-1). Calcite dissolution can, however, neutralize the acidic solutions resulting from the dissolved \( \text{CO}_2 \) and thus reduce pH stress on microbial cells. In addition, utilization of lactate could cause pH decrease in the culture solution. However, we did not observe a significant change of lactate concentrations in the absence or the presence of calcite coupons within 17 h (Figure B.4D).

**B.3.3 MnO$_2$ reduction by stressed cells**

Under anaerobic conditions, MR-1 can use Mn(IV) as an electron acceptor and reduce Mn(IV) (i.e., MnO$_2$) to Mn(II), which becomes aqueous Mn$^{2+}$. In this study, the metabolic function of the stressed MR-1 was evaluated by monitoring the reaction rate of Mn(II) formation when MnO$_2$ was present in the MR-1 cultures. The results suggest that MnO$_2$ dissolution or reduction in the medium (without cells) was negligible (Figure B.5). For the unstressed cells, the aqueous Mn concentration increased linearly with time in the early reaction period, and arrived at the maximum value after 1.5 h (Figure B.5). The stressed cells were also observed to have a capability to reduce Mn(IV), although their reduction rates (4.74 ± 0.25 and 1.66 ± 0.17 µmol/h under \( \text{CO}_2 \) of 150 psi and 300 psi, respectively) were significantly lower than that of unstressed cells (8.33 ± 0.16 µmol/h) (Figure B.5B). These results indicated that \( \text{CO}_2 \) stress did not influence the metabolic function of MR-1: the stressed cells could reduce Mn(IV) immediately after the stress was removed.
Figure B.5. Mn(II) concentration (A) and CFU (B) during MnO₂ reduction by CO₂ stressed and non stressed cell. (▲) control experiment without cells; (●) control experiment with unstressed cells; (○) stressed cells under 100% CO₂, 150 psi for 25 min; (◊) stressed cells under 100% CO₂, 300 psi for 25 min. The error bars are smaller than the symbols, and here unseen.

B.3.4 Modeling bacterial viability under CO₂ stress

To prudently explain the complex influence of high pressure CO₂ on bacterial survival in a dose-time dependent manner, a simple mathematical model was built using the first order growth and decay model given in Eq (1).

\[
\frac{dC}{dt} = k_1C - k_2CP_{CO_2},
\]

where \( C \) is the viable bacterial cell numbers at time \( t \), \( k_1 \) is the specific growth rate (hr\(^{-1}\)), \( k_2 \) is the specific death rate constant (psi\(^{-1}\)hr\(^{-1}\)) under CO₂ stress, and \( P_{CO_2} \) (psi) is the partial pressure of CO₂. \( k_1\cdot C \) describes normal growth without any limiting factors, which follows a simple exponential curve. \( k_2\cdot C\cdot P_{CO_2} \) represents bacterial death, which is limited by the partial pressure of CO₂.
Integrating Eq (1) with the initial conditions as \( t = 0 \) and \( C = C_0 \):

\[
\frac{C}{C_0} = \exp\left(k_1 t - k_2 t P_{\text{co}_2}\right).
\]  

For partial pressures of \( \text{CO}_2 \leq 0.15 \text{ psi} \) and time periods of \( \text{CO}_2 \) stress \( \leq 5 \text{ hr} \) (solid line in Figure B.2), \( k_2 P_{\text{CO}_2} \ll k_1 \); thus Eq (2) reduces to Eq (3):

\[
\frac{C}{C_0} = \exp(k_1^* t).
\]  

Monte Carlo simulation provided by MATLAB (MathWorks, USA) was employed to generate 50 equal-sized data sets for \( C \), and a genetic algorithm was used to fit the model parameters of \( k_1 \), \( k_1^* \), and \( k_2 \) with each simulated data set. According to the experimental data, the growth rates \( k_1 \) and \( k_1^* \), and the death rate \( k_2 \), were calculated to be about \( 0.12 \pm 0.02 \), \( 0.23 \pm 0.02 \), and \( 0.027 \pm 0.007 \), respectively.

The calculated \( C/C_0 \) values using the parameters \( (k_1 = 0.12, k_1^* = 0.23 \text{ and } k_2 = 0.027) \) are plotted as a function of time in Figure B.2. The assessment on the goodness of the model fit was tested based on the minimization of the error between the fitting data and measured data. When the error was the minimal, the fitting data were considered optimal. The measured \( C/C_0 \) data from the above experiments fit well with the calculated values (Figure B.2), which validated the model’s ability to predict the effect of \( \text{CO}_2 \) on microbial survival.

**B.4. Environmental Implications**

The potential impacts of \( \text{CO}_2 \) leakage from geologic sequestration sites on surrounding geological properties and ecological systems are complicated and diverse. For example, \( \text{CO}_2 \)
leakage might not uniformly distribute throughout the GCS site, and bacterial communities could exhibit different responses to CO$_2$ stress. This study simplifies the situation by employing an environmentally relevant bacterium ($S. oneidensis$ MR-1) to represent the microbial ecosystem in response to CO$_2$ stress.

According to a previous study on the Frio geologic carbon sequestration test site, with 10% leakage of injected CO$_2$, the pH of groundwater can change from 6.7 to 5.3 within 20 m from the leak point $^{239}$. This pH change is very similar to that observed in our system. It has been reported that MR-1 can survive in a broad range of fluctuating pH (between 4 and 10 under aerobic conditions, and from 5.6 to 9.4 under oxygen-limited conditions) $^{222, 240}$. This study shows that high pressure CO$_2$ may well damage cells more than the pH effect. In addition, we observed that MR-1 cell growth resumed its normal rate after CO$_2$ exposure was stopped. Further, the stressed MR-1 displayed the MnO$_2$ reduction capability, although the reduction rate was lower. This implies that such a level of CO$_2$ leakage may not significantly influence the self-cleaning capability of groundwater near a GCS site, especially once the stress is removed. Also in soil/sediment systems, bacteria tend to attach on the minerals in the form of biofilm, and the presence of pH buffering minerals, such as calcite and other metal carbonates, could protect microbial ecology systems against CO$_2$ stress. However, the released metal species may also affect groundwater quality and soil/sediment composition by reacting with minerals in the presence of leaking CO$_2$. These reactions merit further study. This study provides fundamental information for an understanding of the impact of CO$_2$ leakage on microbial survival and metal reduction activity. These findings may affect the ecosystems as well as underground sources of drinking water, and also help design a more accurate predictive model of the ecological impacts of leakage.
Acknowledgments

B.W. and H.S. contributed equally to this project. This study was partly supported by grants to Jun lab and Tang lab from the International Center for Advanced Renewable Energy and Sustainability (I-CARES) and The Consortium for Clean Coal Utilization at Washington University. Also, Y.S.J. and Y.H. were partly supported by the U.S. Department of Energy, in association with the Energy Research Frontier Center (EFRC) of Berkeley Lab (under Contract No. DE-AC02-05CH11231). We would like to thank the Nano Research Facility (NRF) at Washington University for the use of SEM.
Supporting Information for Appendix B

Contents: Experimental details

One table (B-S1)

Three figures (B-S1 – B-S3)

Measurement of extracellular polymeric substances (EPS) and membrane integrity. A modified EPS extraction method was utilized to quantify the EPS during experiments: a microbial floc was achieved by centrifuging 5 ml cell cultures at 4,000 rpm for 10 min (4°C). DNA concentration in the supernatant was measured using a spectrophotometer (Nanodrop, Thermo Scientific, USA). Three biological repeats and two technical repeats were conducted for the experiments. After the supernatant was removed, the microbial floc was dispersed in distilled water to keep the total volume of 5 ml. Then 6 µl of formaldehyde (37%) was added and kept for 1 h at 4°C, after which 0.1 ml NaOH (1 M) was added and kept for 3 h at 4°C. After that, the microbial floc solution was centrifuged (13,200 rpm, 20 min, 4°C) to remove the suspended solids. The concentrations of polysaccharides and proteins were analyzed according to methods described by Dubois et al. and Bradford, respectively.

The integrity of the cytoplasmic membrane of cells was determined using a BacLight Live/Dead Kit (Molecular Probes, Invitrogen, USA). Unstressed and stressed cells were harvested by centrifugation and re-suspended in a volume of 0.85% NaCl to adjust the cell density (OD600) to around 0.04~0.05. Then the sample (100 µl) was transferred onto a 96-well flat-bottom micro-plate, and a 100 µl pre-mixed dye solution (50 µl of 10.02 µM SYTO® 9 and 50 µl of 60 µM propidium iodide) was added. The samples were incubated in the dark for 15 min at ambient temperature. Fluorescence was measured with a fluorescence micro-plate reader.
(BioTek, USA); the excitation wavelength was set at 485 nm, and the emission wavelength was set at 490-700 nm. The ratios of fluorescence intensity at 530 nm (indicating living cells) and at 630 nm (indicating dead cells) were calculated \( \frac{F_{530}}{F_{630}} \). The membrane integrity index was defined as \( I = \frac{F_{530}}{F_{630}} \).

**Biological and technical repeats.** Biological and technical repeats are required for the biological experiments in order to provide real and meaningful data since the biological systems are not easily controlled for uniformity. In this study, we conducted our experiment with both biological and technical repeats. For example, when we exposed bacteria to CO\(_2\), we prepared three test tubes filled with a certain volume of bacterial solution in the pressurized reactor. The samples in these three test tubes were “biological” triplets. In addition, we took two samples from each of the tubes, which were called “technical” duplets. Totally, six samples were employed for further analysis.
Figure B-S1. Schematic diagram of bioreactor.
Figure B-S2. *In situ* pH changes in the presence of CO₂ and ratios of viable cells under pH effect and CO₂ stress (n ≥ 3). (♦) 1% CO₂ (150 psi); (●) 100% CO₂ (150 psi); ratios of viable cells: 100±8.6% (pH effect: cultured at pH 6.16 for 1 hr) and 59.1±7.4% (CO₂ stress: under 1% CO₂ stress for 1 hr); 23.2±14.7% (pH effect: cultured at pH 4.86 for 1 hr) and 0.7±0.1% (CO₂ stress: under 100% CO₂ stress for 1 hr).
Figure B-S3. Growth of *S. oneidensis* under CO$_2$ stress (100% CO$_2$, 150 psi) (A) and growth recovery after CO$_2$ stress for 25 min (B) (n $\geq$ 4). (♦) Control; (●) Stressed cells; (■) Stressed cells in the presence of calcite coupons (0.12 g/ml). The error bars are smaller than the symbols, and here unseen.
Table B-S1. Viable cells, EPS production and released intracellular DNA under CO$_2$ stress (100%, 150 psi, 30 min) (n ≥4)

<table>
<thead>
<tr>
<th></th>
<th>Unstressed</th>
<th>Suspended cells after stress</th>
<th>Loosely-attached cell aggregates after stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total CFU</td>
<td>(8.0 ± 0.2) $\times 10^6$</td>
<td>(1.7 ± 0.1) $\times 10^4$</td>
<td>(7.0 ± 0.1) $\times 10^5$</td>
</tr>
<tr>
<td>Protein (mg/g dry biomass)</td>
<td>282 ± 14</td>
<td>619 ± 31</td>
<td>-</td>
</tr>
<tr>
<td>Polysaccharides(mg/g dry biomass)</td>
<td>31 ± 5</td>
<td>24 ± 2</td>
<td>-</td>
</tr>
<tr>
<td>DNA (ng/µl)</td>
<td>17.8 ± 0.3</td>
<td>27.4 ± 2.2</td>
<td>-</td>
</tr>
<tr>
<td>Membrane integrity (F$<em>{530}$/F$</em>{630}$)</td>
<td>2.05 ± 0.18</td>
<td>0.39 ± 0.06</td>
<td>-</td>
</tr>
</tbody>
</table>
Appendix C. Curriculum Vitae

Yandi Hu

Energy, Environmental & Chemical Engineering, Washington University in St. Louis
Brauer Hall 1015, Campus box 1180, One Brookings Drive, St. Louis, MO, 63130
Phone: (314) 570-4200, Email: huyandi@go.wustl.edu

EDUCATION

➢ Ph.D., Washington University in St. Louis, 2013
Department of Energy, Environmental & Chemical Engineering (advisor: Dr. Young-Shin Jun)

➢ M.S., Nankai University, 2008
College of Environmental Science and Engineering (advisor: Dr. Zhipeng Bai)

➢ B.S., Nankai University, 2005
College of Environmental Science and Engineering

PROFESSIONAL & RESEARCH EXPERIENCE

2008 – present Graduate Research and Teaching Assistant

Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis

2005–2008 Graduate Research Assistant

Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control

College of Environmental Science and Engineering, Nankai University

2007–2008 Graduate Research Assistant

Tianjin Research Institute of Water Transport Engineering, China (part-time internship)

2003–2005 Undergraduate Research Assistant

College of Environmental Science and Engineering, Nankai University

2004–2005 Undergraduate Research Assistant

Agro-environmental Monitoring Center, China (part-time internship)

AWARDS & HONORS

2012 Graduate Student Award in Environmental Chemistry, American Chemical Society (ACS)

2011 Outstanding student research podium presentation award, 242nd ACS National Meeting, Denver, CO

2010 Outstanding student research presentation award, 239th ACS National Meeting, San Francisco, CA
2010    DOE full financial support to attend 2010 EFRC All Hands Meeting
2010    DOE full financial support to attend the 12th National School on Neutron and X-ray Scattering, Argonne National Laboratory and Oak Ridge National Laboratory; selected from more than 200 applicants
2007    First Class Graduate Scholarship of Nankai University; the only recipient in my grade
2006    Second Class Graduate Scholarship of Nankai University; the only recipient in my grade
2005    Second Prize for the Undergraduates’ Innovative Project of Nankai University
2001–2004  Undergraduate Scholarship of Nankai University   (4 times)

**PEER REVIEWED PUBLICATIONS**

Based on research performed during my Ph.D. studies


7.    A.V. Radha, Alejandro Fernandez-Martinez, Yandi Hu, Young-Shin Jun, Glenn A. Waychunas, and Alexandra Navrotsky. Energetic and structural studies of the amorphous Ca\(_1\)\(_{1-x}\)Mg\(_x\)CO\(_3\)\(_{1-x}\)\(_{-x}\)O \((0 \leq x \leq 1)\) systems. Geochimica et Cosmochimica Acta, 2012, 90, 83-95


Based on research performed during my M.S. studies


Based on research performed during my undergraduate studies:


CONFERENCE PROCEEDINGS & PRESENTATIONS

Yandi Hu and Young-Shin Jun, “Effects of Anions on Heterogeneous Hydrous Fe(III) Oxides Precipitation on Quartz”, American Chemical Society (ACS) Spring Meeting, New Orleans, April 2013


Yandi Hu and Young-Shin Jun, “Roles of nano- and micro-scale subsurface geochemical reactions on safe and efficient GCS operations”, Washington University in St. Louis, March 2013 (invited talk)

Yandi Hu and Young-Shin Jun, “Na+, Ca2+, and Mg2+ in Brines Affect Biotite Dissolution, Surface Cracking, and Illite Precipitation under Hydrothermal Conditions”, American Geophysical Union (AGU) Fall Meeting, San Francisco, December 2012


Yandi Hu and Young-Shin Jun, “Effects of Temperature, CO2(aq), and Cations on Biotite Dissolution and Secondary Mineral Formation”, American Geophysical Union (AGU) Fall Meeting, San Francisco, December 2010


Yandi Hu and Zhipeng Bai, “Probability Health Risk Assessment on Human Exposure to Environmental Polycyclic Aromatic Hydrocarbons in Tianjin, China”, International Symposium on Ambient Air Particulate Matter Techniques and Policies for Pollution Prevention and Control, Tianjin, China, July 2007

Yandi Hu and Zhipeng Bai, “Source Apportionment of Ambient Aerosol Samples by Radial Basis Function Neural Network”, Atmospheric Sciences and Applications to Air Quality (ASAAQ), Hong Kong, China, 2007

References

17. Shao, H.; Ray, J. R.; Jun, Y.-S., Dissolution and precipitation of clay minerals under 

18. Cole, D. R.; Chialvo, A. A.; Rother, G.; Vlcek, L.; Cummings, P. T., Supercritical fluid 
behavior at nanoscale interfaces: Implications for CO\textsubscript{2} sequestration in geologic formations. Philos. Mag. 2010, 90, (17-18), 2339-2363.

19. Kalinowski, B. E.; Schweda, P., Kinetics of muscovite, phlogopite, and biotite 

Knauss, K. G., Potential environmental issues of CO\textsubscript{2} storage in deep saline 
aquifers: geochemical results from the Frio-I Brine Pilot test, Texas, USA. Appl. Geochem. 2009, 
24, (1106-1112).

on Geochemistry: Surface and Groundwater, Weathering, and Soils, Elsevier: San Diego, 2003; 
Vol. 5.

22. Shao, H.; Ray, J. R.; Jun, Y.-S., Dissolution and precipitation of clay minerals under 
geologic CO\textsubscript{2} sequestration conditions: CO\textsubscript{2}-brine-phlogopite interactions. Environ. Sci. 

23. Shao, H.; Ray, J. R.; Jun, Y.-S., Effects of salinity and the extent of water on supercritical 
2011, 45, (4), 1737-1743.

between supercritical carbon dioxide and NaCl brine: relevance to the integrity of a geologic 

25. Gaus, I.; Azaroual, M.; Czernichowski-Lauriol, I., Reactive transport modelling of the 
impact of CO\textsubscript{2} injection on the clayey cap rock at Sleipner (North Sea). Chem. Geol. 2005, 217, 
(3-4), 319-337.

26. Sugimori, H.; Iwatsuki, T.; Murakami, T., Chlorite and biotite weathering, Fe\textsuperscript{2+}-rich 
corrnsite formation, and Fe behavior under low P\textsubscript{O\textsuperscript{2}} conditions and their implication for 

and mechanisms in the laboratory and in nature: Early stage weathering environment and 

dissolution processes of biotite: implications for Fe behavior during Archean weathering. Earth 

29. Dong, H. L.; Peacor, D. R.; Murphy, S. F., TEM study of progressive alteration of 
62, (11), 1881-1887.

Acta 2005, 69, (2), 399-413.

31. He, Y. T.; Bigham, J. M.; Traina, S. J., Biotite dissolution and Cr(VI) reduction at 


65. Breen, K. J. *USGS water resources investigation report (84-4314), Ohio department of natural resources division of oil and gas.; 1985.


