Essays on Entrepreneurship

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Coupling of Geochemical Reactions and Geophysical Properties of Clay Minerals in Energy-related Subsurface Engineered Systems

by
Lijie Zhang

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

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ABSTRACT OF THE DISSERTATION

Coupling of Geochemical Reactions and Geophysical Properties of Clay Minerals in Energy-related Subsurface Engineered Systems

by

Lijie Zhang

Doctor of Philosophy in Energy, Environmental and Chemical Engineering

Washington University in St. Louis, 2018

Professor Young-Shin Jun, Chair

Engineered subsurface operations, such as geologic CO\(_2\) sequestration (GCS) and CO\(_2\)-enhanced unconventional oil/gas recovery, are promising strategies to mitigate global warming and meet energy demands. At subsurface sites, CO\(_2\)-saturated brine–mineral interactions can be affected by aqueous species, either naturally existing or injected, and the interactions may further affect the geophysical properties of rocks and minerals, such as their porosity, permeability, and wettability. Such geophysical properties can control the sealing integrity of the caprock layer, which is essential to safe and efficient long-term CO\(_2\) storage. Moreover, the flow and transport of fluids at subsurface sites are also influenced by the geophysical properties. Therefore, to ensure safer and more efficient engineered subsurface operations, it is important to have a better understanding of the coupling of geochemical reactions of rocks and minerals and their geophysical properties under conditions relevant to subsurface environments.

In this work, clay minerals (phyllosilicates) are used as model minerals because of their abundance at subsurface sites used for energy-related engineered operations. The subsurface brine
has high salinities, so we first identified the interplay between salinity-induced chemical reactions of biotite (an Fe-bearing mica) and its wettability alteration under high temperature and high pressure conditions. In characterizing the surface physico-chemical properties of reacted biotite, we found that biotite dissolution was enhanced at higher salinities, and biotite surfaces were rougher, more negatively charged, and contained higher densities of hydroxyl groups. All these changes in surface properties made biotite more hydrophilic.

Second, in addition to salinity, we examined the effects of organic and inorganic oxyanions on brine–biotite interactions. Regarding the effects of short-chain carboxylic acid anions, acetate slightly inhibited biotite dissolution and promoted secondary mineral precipitation, mainly due to pH-induced aqueous acetate speciation (mainly acetic acid) and the subsequent surface adsorption of acetic acid to biotite surface Si and Al sites. However, oxalate strongly enhanced biotite dissolution and induced faster and more significant surface morphology changes by forming bidentate mononuclear surface complexes. Our experimental results showed that oxalate selectively attacks edge surface sites and enhances biotite dissolution, thus it increases the relative reactivity ratios of biotite edge surfaces to basal surfaces, while acetate does not impact this relative reactivity. The information on the reactivity differences at biotite edge and basal planes in the presence of organic ligands has implications for subsurface operations in organic-rich sites. Next, we investigated brine–biotite interactions in the presence of inorganic phosphate, which strongly precipitates metal ions. At 95 °C and 102 atm of CO₂, biotite dissolution was four times higher with 10 mM phosphate than with the control, 0.1 mM, and 1 mM phosphate. Despite their dissolution differences, in all the phosphate systems, phosphate interacted with Al and Fe, forming surface complexes and precipitating as Fe- or Al-bearing minerals on surfaces and in solutions.
The biotite basal surfaces became more hydrophilic after reaction with phosphate, mainly as a result of phosphate adsorption.

Third, we further expanded our investigation into the interactions between clay minerals and phosphonates, which are commonly used as scale inhibitors during engineered subsurface operations. These phosphonates can degrade to increase phosphate concentrations in formation water. We observed that the phosphonate groups enhanced biotite dissolution through both aqueous and surface complexations with Fe, with more significant effects at a higher phosphonate concentration. In particular, surface complexation was more dominant with phosphonates with fewer phosphonate functional groups, and aqueous complexation played a more important role in the presence of phosphonates with more functional groups. The presence of phosphonates also promoted secondary precipitation of Fe- and Al-bearing minerals both in the solution and on the reacted biotite surfaces. Moreover, phosphonate structure (i.e., the number of phosphonate functional groups) affected the distribution, morphology, and phases of secondary precipitates. As a result of phosphonate adsorption, biotite basal surfaces were altered to be more hydrophilic. Next, to better understand the fate and transport of phosphonate scale inhibitors, we elucidated the roles of Fe-bearing phyllosilicates on the chemical stability of phosphonates under subsurface relevant conditions. Three phyllosilicate minerals were tested, showing different effects on DTPMP (diethylenetriaminepenta(methylene)phosphonate) degradation. Muscovite (an Fe-poor phyllosilicate) did not have distinguishable effects on DTPMP degradation. Nontronite (an Fe(III)-rich phyllosilicate) showed slightly promotion effects, and biotite (an Fe(II)-rich phyllosilicate) notably promoted DTPMP degradation. We found that structural Fe(II) within phyllosilicates is key to the redox degradation of DTPMP: Reactive oxygen species (ROS) were generated through
the reduction of molecular oxygen by Fe(II) in biotite, and the ROS further degraded DTPMP to form phosphate, formate, and new phosphonates.

Information provided by this study advanced our understanding of the geochemical reactions of clay minerals in the presence of naturally existing aqueous species and the chemical additives introduced during engineered subsurface operations, and illuminated their impacts on the wettability alterations of clay minerals. The findings will help bridge the knowledge gaps between chemical reactions and geophysical property changes of minerals, and they have important implications for designing safer and more efficient energy-related engineered subsurface operations.
Chapter 1. Introduction

1.1 Background

1.1.1 Geologic CO₂ Sequestration (GCS) and CO₂-enhanced Unconventional Oil/Gas Recovery

Engineered subsurface operations, such as geologic CO₂ sequestration (GCS), oil/gas recovery, geothermal program, nuclear storage, have received increasing attention as promising strategies to mitigate global warming, meet energy demands, and manage wastes. GCS is operated by injecting and storing CO₂ in subsurface sites to reduce anthropogenic CO₂ emission to the atmosphere.¹⁻³ Of the several possible types of GCS sites, including nearly depleted oil or gas reservoirs, deep oceans, unmineable coal seams, and deep saline aquifers, deep saline aquifers are estimated to have the greatest capacity for carbon storage and sequestration.¹ In addition, led by new applications of horizontal drilling and hydraulic fracturing, CO₂-enhanced unconventional oil and gas recovery from shale reservoirs has been rapidly growing as a means of oil/gas production, and this operation can also be eventually used for storing CO₂.²⁻⁴ The field sites for these energy-related engineered subsurface operations are usually deeper than 800 m, where the temperature and pressure can range from 31 °C to 110 °C and from 73.8 atm to 600 atm, respectively.⁵⁻⁷ Under these temperature and pressure conditions, CO₂ is in its supercritical phase. In this dissertation, we will focus on these two CO₂-involved processes, which share similar CO₂ storage processes and are operated in similar subsurface environments.
After CO$_2$ is injected, multiple processes can occur to store CO$_2$ at subsurface sites (Figure 1.1). The upward movement of CO$_2$ will be typically hindered by low permeability caprocks (structural trapping). There is CO$_2$ stored in porous formation rocks by capillary forces when it replaces brine and again replaced by brine (residual trapping). The injected CO$_2$ will dissolve into brine in the reservoirs (solubility trapping) and it can also precipitate as carbonate minerals (mineral trapping), leading to CO$_2$ storage.$^8$-$^9$ The interactions among CO$_2$, brine, and minerals can affect the storage processes of CO$_2$, thus influencing the safety and efficiency of CO$_2$ sequestration operations. Hence, it is important to understand the geochemical reactions of rocks and minerals under subsurface relevant conditions.

![Figure 1.1 CO$_2$ storage processes.$^9$](image)

**1.1.2 Brine–mineral Interactions under Conditions Relevant to Subsurface Operations**

Shales are abundant in reservoirs for unconventional oil/gas recovery,$^{10}$-$^{11}$ and they have also served as host rocks and caprocks for CO$_2$ storage.$^1$,$^{12}$ Along with fine grains of
quartz, feldspars, and calcite, various clay minerals (phyllosilicates) are main constituents of shales, with a minimum mass fraction of about 40%.\textsuperscript{13-16} The low permeability of clay minerals plays an important role in the sealing of caprock shales. Because of their abundance and important role during engineered subsurface operations, clay minerals were investigated in this study. The mica group is an important family of phyllosilicate minerals, and the mica contents of representative shales in CO\textsubscript{2} sequestration sites are shown in Table 1.1. Biotite (Fe-rich), which is a reactive mica mineral, and its weathering product, glauconite, have been reported to be present in several energy-related subsurface operation sites.\textsuperscript{17} Muscovite (Fe-poor) is the most common form of mica. Therefore, biotite and muscovite were chosen as model mica minerals. In addition, nontronite (Fe-rich, smectite group of clay minerals) was also used. These three phyllosilicate minerals share similar layered structures, containing framework cations occupying tetrahedral sheets and octahedral sheets and interlayer cations to balance the charge (Figure 1.2). They have anisotropic structures consisting of basal planes and edge planes, and edge planes are reported to be more reactive than basal planes.\textsuperscript{18-21}

<table>
<thead>
<tr>
<th>Sites</th>
<th>Norway Sleipner</th>
<th>Australia Muderong</th>
<th>United Kingdom Kimmeridge</th>
<th>Canada Venture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mica (wt%)</td>
<td>30%</td>
<td>17%</td>
<td>20%-25%</td>
<td>10%-33%</td>
</tr>
</tbody>
</table>

Aqueous chemistry at subsurface sites is considerably different from surface water chemistry. As injected CO\textsubscript{2} dissolves, the brine at subsurface sites is acidified to pH ~3, and it could be further acidified to pH ~1 due to dissolution of co-injected acidic gases, such as H\textsubscript{2}S and SO\textsubscript{2}.\textsuperscript{23} In deep saline aquifers, brines have reported salinities ranging from
several mg/L to several hundred g/L. In brine, sodium (Na⁺) is the most abundant cation, constituting 70%–90% of the total mass of cations. Inorganic and organic anions are also found in formation brines, such as sulfate (0.01–0.05 M) and phosphate (0.5–20 µM), and acetate (0.016–0.25 M) and oxalate (0–5 mM). Because supercritical CO₂ (scCO₂) is a good organic solvent, the concentrations of some organic compounds (mainly formate and acetate) can increase even after CO₂ injection, as reported in a recent study on the Frio formation. In addition to these naturally existing aqueous species, chemical additives are injected into subsurface sites during engineered operations. Among the chemical additives, scale inhibitors, at an average concentration of ~0.023 wt.%, are utilized to inhibit the formation of scale minerals, which can reduce the porosity and permeability of wellbores and the cracked reservoir rocks, or block flow in production wells.

Figure 1.2 Crystal structure shared by biotite, muscovite, and nontronite. The grey balls indicate interlayer cation, blue and yellow balls indicate tetrahedral (T) cations, and brown and light blue balls indicate octahedral (O) cations.
However, information is limited on the effects of subsurface conditions on brine–mineral interactions. Clay minerals can undergo geochemical reactions, including mineral dissolution and subsequent secondary mineral precipitation, through several mechanisms. The release of interlayer cations occurs mainly through ion-exchange reactions with aqueous protons or cations. The dissolution of framework cations is through proton-mediated or ligand-mediated mechanisms. Aqueous species forming complexes with released metal ions can also mediate mineral dissolution by reducing the activity of aqueous metal ions. Moreover, the dissolution of minerals releasing metal ions will change the saturation states in the solutions, leading to secondary mineral precipitation. These geochemical reactions of minerals can be influenced by the aqueous chemistry conditions at subsurface sites, such as high salinity and abundant naturally existing or injected chemicals. The presence of aqueous species may also change the reactivities of the edge planes and basal planes of clay minerals. Moreover, the geochemical reactions of minerals may further affect the geophysical properties of rocks, which are important for CO₂ storage and fluid transport.

1.1.3 Importance of Coupling Geochemical Reactions and the Geophysical Properties of Minerals

During CO₂ storage, capillary pressure is important in structural trapping and residual trapping of CO₂. Capillary pressure \( P_c \) is defined as the pressure difference between the wetting phase (water, \( P_w \)) and non-wetting phase (scCO₂, \( P_{CO2} \)). To store CO₂ in porous reservoir rocks initially occupied by brine, the CO₂ pressure must exceed the capillary pressure and displace the brine; later, brine can again substantially replace CO₂,
leaving some trapped in the pore spaces by capillary forces.\textsuperscript{35-37} On the other hand, if the CO\textsubscript{2} pressure exceeds the capillary pressure in the caprock layer, its sealing will fail and CO\textsubscript{2} will leak. As denoted by the Young-Laplace equation,

\[ P_c = P_{CO2} - P_w = \frac{2\gamma_{wc} \cos \theta}{R}, \]

the capillary pressure is dependent on the scCO\textsubscript{2}–brine interfacial tension ($\gamma_{wc}$), pore radius ($R$ indicates porosity and permeability), and contact angle ($\theta$ indicates wettability).

An outstanding scientific question regarding CO\textsubscript{2} storage is the extent to which mineral dissolution and secondary mineral precipitation processes affect the rock’s geophysical properties (porosity, permeability, and wettability), determining the long-term storage of CO\textsubscript{2}. Interactions among scCO\textsubscript{2}, brine, and rock may change the geophysical properties of reservoirs,\textsuperscript{38-43} thus affecting CO\textsubscript{2} trapping mechanisms and the transport of related fluids. Saraji et al. investigated the wettability of a scCO\textsubscript{2}–water–quartz system under reservoir conditions and reported that, compared to subcritical CO\textsubscript{2}, scCO\textsubscript{2} changes quartz surfaces toward less water-wet conditions.\textsuperscript{42} Furthermore, wettability depends on reservoir temperature, pressure, and brine salinities. However, there are few studies investigating the impacts of chemical reactions on wettability changes of caprock minerals.

Moreover, maintaining a proper level of porosity and permeability is important in unconventional oil/gas recovery. In this process, fracking fluids are pumped into wellbores, cracking the reservoir shale to release brine, gas, and petroleum and to make them flow more freely. Shiraki et al. conducted core-flooding laboratory experiments to study water–rock interactions during CO\textsubscript{2} flooding in the Tensleep Formation, Wyoming, USA. They reported that core permeability decreased by 31–44\% within 7 days because of kaolinite crystal growth in pore throats, despite dolomite dissolution.\textsuperscript{41} Dissolution of minerals can
create void spaces, and secondary mineral precipitation can plug pore throats: both of these phenomena affect porosity and permeability. Hence, a better understanding about the coupling of geochemical reactions and the geophysical properties of minerals is important for effective CO₂ storage and fluid transport.

1.2 Research Objectives and Tasks

1.2.1 Current Knowledge Gaps

Clay minerals are abundant in subsurface reservoirs and play an important role in the sealing of the caprock layer.¹ ¹⁰⁻¹² For safer and more efficient energy-related engineered subsurface operations, it is essential to have a comprehensive understanding of the brine–clay mineral interactions under relevant subsurface conditions. Moreover, information is needed on the relationship between brine–clay mineral chemical reactions and mineral geophysical properties, which determines the storage of CO₂ and the transport of related fluids.

Salinity is high in subsurface brine, and it can directly affect mineral wettability by changing interfacial tension.⁶ The high salinity can promote mineral dissolution, and salinity-induced chemical reactions can change mineral surface properties, which impact mineral surface wettability. However, no previous studies have systematically examined the effects of chemical reactions on mineral wettability alterations under subsurface relevant conditions. Such studies can help identify the factors that can be used to link geochemical reactions and geophysical properties of minerals.

Furthermore, information is limited on the distinctive reactivities of the crystal planes of clay minerals in the presence of organic ligands. Organic ligands can form
complexes with specific mineral surface sites, affecting the relative reactivity of different crystal planes. At subsurface sites, faults and fractures in the caprock layer are often reported,\textsuperscript{44-46} which expose active edge surfaces to the surrounding environment and can contribute to dissolution. When dissolution occurs more significantly at edge planes, this preferential reactivity can affect the transport of injected CO\textsubscript{2} at subsurface sites. Hence, it is critical to investigate the impacts of anisotropic structure on geochemical reactions of clay minerals, especially in the presence of organic ligands.

Phosphate is an important inorganic oxyanion ligand to study. Phosphate naturally exists in subsurface brines at low concentrations of 0.5–20 µM,\textsuperscript{47} and its concentration can be increased significantly, to 1–2 mM, during energy-related engineered subsurface processes.\textsuperscript{48-49} Under ambient conditions, phosphate readily forms surface complexes and adsorbs onto mineral surfaces.\textsuperscript{50-52} In addition, phosphate can precipitate with aluminum or iron ions in acidic solutions or oils.\textsuperscript{53-54} It is expected that phosphate will interact with mineral surfaces and metal ions in the solutions, affecting brine–mineral interactions. Besides, surface interactions between phosphate and minerals may change the mineral surface properties, altering wettability. However, detailed information about the effects of phosphate on brine–mineral interactions and the consequent wettability alteration is lacking.

In addition to naturally existing aqueous species, phosphonate-based scale inhibitors are common chemical additives during engineered subsurface operations, and they can be degraded to increase phosphate concentrations.\textsuperscript{48-49} Phosphonates have a high affinity for mineral surfaces, resulting in their loss in brine and affecting their performance in mineral scale inhibition. Nonetheless, the effects of phosphonate concentrations and
their structures on brine–mineral interactions are unclear, as is the consequent wettability alteration of minerals. On the other hand, brine–mineral interactions can also impact the chemical stability of phosphonates. Still, there is little information about the chemical stability of phosphonates under subsurface relevant conditions.

1.2.2 Specific Objectives and Tasks

In order to fill the knowledge gaps of coupling the geochemical reactions of clay minerals with mineral geophysical property alterations (specifically focusing on wettability), the following objectives and tasks are specified.

Objective 1: Determine the interplays between salinity-induced chemical reactions and wettability alterations of clay minerals under subsurface relevant conditions.

Hypothesis 1: Mineral wettability is related to mineralogy, surface morphology, and surface properties (e.g., roughness, surface charge, and functional groups). Salinity can promote dissolution of clay minerals by enhancing ion-exchange reactions with interlayer cations. The salinity-induced dissolution will change the surface morphology and surface properties of minerals (e.g., functional groups and surface charge). By considering these changes, we can determine the interplays between chemical reactions and the wettability alterations of minerals.

Objective 2: Investigate the effects of organic and inorganic oxyanions on brine–clay mineral interactions under subsurface relevant conditions.

Hypothesis 2: Organic and inorganic oxyanions in brine can make complexes with aqueous metal ions or with metal sites on mineral surfaces, thus promoting or inhibiting
mineral dissolution. Clay minerals have an anisotropic structure with basal surfaces and edge surfaces, and the edge surfaces are much more reactive than the basal surfaces. Thus, the dissolution of clay minerals will preferentially occur at their edges. By making complexes with specific surface sites, oxyanions can change the relative reactivity of edge surfaces to basal surfaces. Inorganic phosphate can complex with surface sites and precipitate with aluminum or iron ions, either in aqueous solutions or on mineral surfaces. The enhanced secondary mineral precipitation may further trigger biotite dissolution. Phosphate surface adsorption, mineral dissolution, and surface precipitation of secondary minerals will all affect mineral surface morphology and surface properties, and thus alter mineral wettability.

**Objective 3:** Elucidate the effects of phosphonate concentrations and phosphonate structures on the interactions between clay minerals and phosphonate-based scale inhibitors, and examine the chemical stability of phosphonates.

**Hypothesis 3:** Phosphonates are strong chelating agents that can form aqueous complexes with metal ions in solutions or form surface complexes with metal sites on minerals. Phosphonate concentrations and phosphonate structures affect the extent and strength of aqueous complexation and surface complexation, thus further influencing mineral dissolution and secondary mineral precipitation. The chemical stability of phosphonates can also be impacted by the reactivity of clay minerals. In particular, the Fe(II) sites in clay minerals can react with molecular oxygen to form reactive oxygen species to degrade phosphonates.
1.3 Dissertation Overview

To realize the three objectives described, three tasks were completed, with each task corresponding to an objective. **Task 1** determined the interplays between salinity-induced chemical reactions and wettability alteration of biotite by considering the surface property changes caused by chemical reactions. **Task 2** investigated the effects of organic and inorganic oxyanions on brine–clay mineral interactions and clarified the mechanisms of their effects. **Task 3** elucidated the interactions between clay minerals and phosphonate-based scale inhibitors, evaluating the influences of phosphonate concentrations and phosphonate structures. Further, it examined the chemical stability of phosphonates affected by the reactivity of clay minerals and illuminated the degradation mechanisms of phosphonate-based scale inhibitors in the presence of biotite. **Figure 1.2** shows an overview of the tasks and related chapters.

**Figure 1.2** Overview of dissertation tasks and related chapters.
**Task 1**, linking salinity-induced chemical reactions and the wettability alterations of biotite, is presented in **Chapter 2**. At 95 °C and 102 atm of CO₂, biotite dissolution experiments were conducted in solutions with salinities of 0, 0.1, 0.5, and 1.0 M NaCl, simulating subsurface conditions. Surface properties of the reacted biotite were characterized, and static and dynamic water contact angles on reacted biotite basal surfaces were measured under high temperature and high pressure conditions. We successfully identified surface physico-chemical property changes and qualitatively linked them to wettability alterations.

**Task 2**, exploring brine–clay mineral interactions in the presence of organic and inorganic oxyanions, is addressed in **Chapters 3** and 4. In **Chapter 3**, to study the effects of short-chain carboxylic acid anions, biotite was reacted with 10 and 50 mM acetate and oxalate at 95 °C and 102 atm of CO₂. Aqueous solutions and solid samples were analyzed, and quantitative analyses of dissolution differences between biotite edge and basal planes were made. Knowing the mechanisms of the effects of acetate and oxalate on the relative reactivities of biotite edge and basal planes can help predict the dissolution of clay minerals with other inorganic and organic ligands. **Chapter 4** investigates the interactions between inorganic phosphate and biotite. The effects of phosphate on biotite dissolution and secondary mineral precipitation were investigated within a wide concentration range of 0–10 mM, focusing on the evolution of aqueous cations, biotite surface morphology, and secondary mineral phases. In addition, the contact angles of the reacted biotite samples were analyzed under both ambient conditions and high temperature and high pressure conditions. The factors resulting in the wettability alterations of biotite with phosphate were identified.
Task 3, examining interactions between organic phosphonate-based scale inhibitors and clay minerals, is addressed in Chapters 5–7. Chapters 5 and 6 describe biotite dissolution experiments conducted under subsurface relevant conditions (95 °C and 102 atm CO₂), and give the results of aqueous and solid analyses to understand biotite dissolution and secondary mineral precipitation processes. Contact angle measurements quantified the effects of phosphonate–mineral interactions on wettability alteration. The mechanisms of aqueous complexation, surface complexation, the formation of secondary minerals, and wettability alteration are discussed. Chapter 5 investigates the effects of phosphonate concentrations (0–1.0 mM) on brine–biotite interactions, using diethylenetriaminepenta(methylene)phosphonate (DTPMP) as a model phosphonate scale inhibitor. Chapter 6 examines the effects of phosphonate structures, emphasizing the number of phosphonate functional groups, on brine–biotite interactions. Furthermore, the chemical stability of phosphonates affected by the reactivity of clay minerals and their mechanisms are presented in Chapter 7. The degradation of phosphonate was investigated in the presence of three clay minerals: an Fe-poor muscovite, an Fe(II)-rich biotite, and an Fe(III) rich nontronite. The chemical stability of phosphonate was coupled with the reactivity of Fe-bearing clay minerals. Additionally, Chapter 8 reports sulfate’s effects and its comparison with those of other inorganic/organic ligands discussed in previous chapters.
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Chapter 2. Effects of Salinity-Induced Chemical Reactions on Biotite Wettability Changes under Geologic CO₂ Sequestration Conditions

The results of this chapter have been published in Environmental Science & Technology Letters, 2016, 3(3), 92-97.

Abstract

The wettability of rocks and minerals significantly affects the safety and efficiency of energy-related subsurface operations. However, the interplays between chemical reactions and wettability alterations have received only limited attention until now. To address this knowledge gap, in this chapter, we describe our study of the effects of salinity-induced chemical reactions on biotite’s wettability changes under relevant subsurface conditions. Biotite was reacted at 95 °C and 102 atm of CO₂ for 70 h in solutions with salinities of 0, 0.1, 0.5, and 1.0 M NaCl. Then, static and dynamic water contact angles on the reacted biotite basal surfaces were measured using a captive drop method. As a result of enhanced biotite dissolution at higher salinities, increased roughness, more negatively charged surfaces, and higher densities of hydroxyl groups on the biotite surfaces made biotite basal surface more hydrophilic. These results provide new information about the
interplay of chemical reactions and wettability alterations of minerals, providing a better understanding of CO₂ transport in subsurface environments.

2.1 Introduction

In geologic CO₂ sequestration (GCS), the wettability of the reservoir rocks and minerals affects the mobility, residual trapping capacity, and caprock breakthrough pressures of the injected supercritical CO₂ (scCO₂). Previous experimental and modeling studies have shown that scCO₂, temperatures, pressures, and aqueous chemistries, such as salinity, all impact the wettability of the rocks and minerals. For example, Chiquet et al. reported a transition from water-wet toward intermediate wettability for mica and quartz with increasing CO₂ pressures, and mica showed a more pronounced wettability alteration.

Although the wettability of rocks and minerals has been widely investigated, the results show considerable uncertainties. In CO₂/water/silica systems, Jung et al. reported an increase in contact angles (CAs) with increasing salinity in the range of 0–5 M, whereas Wang et al. found a slight decrease in the range of 0–1.2 M. Both constant and increasing CAs with higher CO₂ pressures were reported for silica. These uncertainties can result from varying surface roughnesses, surface contaminations, or surface chemical reactions during measurements. Mineral dissolution and secondary phase precipitation were observed even within a short time at field sites and in laboratory studies under GCS conditions. In addition to direct effects of salinity on wettability caused by interfacial tension, salinity-induced chemical reactions can change mineral surface properties, thus affecting wettability. However, no studies have systematically
examined the effects of chemical reactions on mineral wettability alterations under GCS relevant conditions.

Deep saline aquifers are estimated to have a large capacity for CO$_2$ storage.$^{1,70-72}$ They contain highly saline brine, with Cl$^-$ generally falling in the range of 0.01–2.2 M.$^{26}$ For example, the Frio-I GCS site has a Na–Ca–Cl type brine with a salinity of ~1.6 M.$^{26}$ At the Weyburn CO$_2$-enhanced oil recovery site, the Cl$^-$ concentration ranges from 0.4 to 1.0 M.$^{73}$ In addition, salinity compresses the electrical double layer, impacting wettability.$^6$ Salinity also affects mineral dissolution and secondary mineral formation.$^{75-76}$ Hence, the effects of salinity on mineral wettability alteration have been studied; however, the effects of salinity-induced chemical reactions on wettability changes have not been investigated.$^{38-39,43,60}$

Therefore, this study, conducted under conditions relevant to energy-related subsurface operations, seeks to systematically relate salinity-induced chemical reactions of biotite, a model mineral in caprocks, with subsequent wettability changes, and to elucidate the mechanisms of wettability changes. Our findings will fill the urgent need to understand the unexplored relationships among salinity, chemical reactions, and wettability changes of minerals and thus will provide benefits for environmentally sustainable CO$_2$ storage.

### 2.2 Experimental Section

#### 2.2.1 Minerals and Chemicals

Biotite (Ward’s Natural Science) was cleaved along the {001} basal plane to 80 ± 10 µm thick flakes that were cut into 2.5 cm × 2.5 cm squares. The biotite flakes were sonicated with acetone, ethanol, and isopropanol to remove organic matter, then rinsed
with deionized (DI) water, and dried with high-purity nitrogen gas. Clean biotite specimens were also ground using stainless steel blades and sieved to yield particles with sizes of 53–106 µm for further powder dissolution experiments. The chemical composition of biotite was analyzed with X-ray fluorescence and is shown in Table 2.1. The chemical formula for biotite is \( \text{K}_{0.91}\text{Na}_{0.08}\text{Ca}_{0.005}(\text{Mg}_{0.57}\text{Mn}_{0.02}\text{Fe}_{0.37}\text{Ti}_{0.04})_3(\text{Al}_{1.00}\text{Si}_{3.00})_3\text{O}_{10}(\text{F}_{0.51}\text{(OH)}_{0.49})_2 \). A more detailed explanation is available in section 2-S1 of the Supporting Information for Chapter 2.

**Table 2.1** Chemical composition of biotite used in this study, analyzed with X-ray fluorescence (XRF) (unit: wt%).

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>TiO₂</th>
<th>MnO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>CaO</th>
<th>Others (H, F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRF</td>
<td>39.0</td>
<td>11.1</td>
<td>17.5</td>
<td>13.9</td>
<td>2.19</td>
<td>0.84</td>
<td>9.4</td>
<td>0.6</td>
<td>0.1</td>
</tr>
</tbody>
</table>

All chemicals used were at least ACS grade, and solutions were prepared in deionized (DI) water (> 18.2 MΩ·cm, Barnstead, Dubuque, IA). Based on reports from GCS field sites, the salinities are always high and the concentrations of \( \text{Cl}^- \) range from 0.01 to 2.2 M.\(^{26,77}\) Therefore, 0, 0.1, 0.5, and 1.0 M \( \text{NaCl} \) solutions were chosen as the experimental conditions to simulate the salinity relevant to GCS sites.

### 2.2.2 High Temperature and High Pressure Batch Experiments

Biotite flake and powder dissolution experiments were conducted in a 300 mL high temperature and high pressure reactor (Parr Instrument Co.), as used in our previous studies (Figure 2.1).\(^{65-66,78-79}\) During dissolution experiments, the temperature was set at 95 °C and pressure was maintained at 102 atm \( \text{CO}_2 \).\(^{79-80}\) This pressure is representative of the pressure condition at about 1 km depth.\(^{80}\) The temperature is relatively higher than the
temperature at about 1 km deep, however, it helped to trigger chemical reactions and allowed for observations within short experimental time scales. The initial pH was calculated by GWB (Geochemists’ Workbench, Release 8.0, RockWare, Inc). The thermo.com.V8.R6+.dat database was chosen for the calculation. In the database, the B-dot equation was used to calculate the activity coefficients of the aqueous species at high ionic strength. The fugacity of 102 atm CO$_2$ was recalculated to be 76.5 atm using Duan and Sun’s equation.$^{81}$ Under our experimental conditions (95 °C, 102 atm CO$_2$), the initial pH was around 3.16.

For flake dissolution, three biotite flakes and 40 mL of prepared solutions with different salinities (0, 0.1, 0.5, and 1.0 M NaCl) were put in 50 mL PTFE tubes. The tubes were covered with Teflon tape with four perforations in it and placed in the reactor. For powder dissolution experiments, 0.15 g of biotite powder with sizes ranging between 53–106 µm and 40 mL of solution were put directly in the 300 mL polytetrafluoroethylene lined reactor. The suspensions were stirred.

*Figure 2.1 Experimental setup for the high temperature and high pressure batch experiments.*
Batch experiments were stopped after reaction for 70 h. The aqueous solutions from flake dissolution were filtered through a 0.2 μm polypropylene membrane and acidified in 1% trace metal nitric acid (HNO₃). The dissolved ion concentrations were then analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 7300 DV). The reacted biotite flakes were carefully rinsed with DI water, dried with high purity nitrogen, and then immediately stored in tubes to avoid any contamination. All samples were treated the same way.

2.2.3 Contact Angle Measurements

Contact angles on prereacted biotite basal surfaces were measured using a captive drop method in a high-pressure and high-temperature CA measurement chamber (Figure 2, Temco, IFT-10), as done in previous work by Jung and Wan. During the measurement, the temperature and pressure of the chamber were kept at 48 ± 1 °C and 102 atm of CO₂, respectively. The temperature was considerably lower than the reaction temperature (95 °C) to retard any biotite dissolution during CA measurements (Figure 2-S1). Both static and dynamic CAs were measured by generating a CO₂ bubble on a biotite basal surface. ImageJ, combined with DropSnake and Low-Bond Axisymmetric Drop Shape Analysis (LB-ADSA) plugins, was used to analyze the CAs. As a convention, the CA values reported hereafter refer to the water phase. The lowest and largest CAs during dynamic CA measurements were reported as the receding (θ₉) and advancing (θₐ) CAs, respectively. The length of the contact line was measured from the CO₂ receding images. A detailed process of CA measurements can be found in 2-S2.
2.2.4 Characterization of Reacted Biotite

Biotite basal surface morphology and roughness were then examined via atomic force microscopy (AFM) (Nanoscope V Multimode, Veeco). Under ambient conditions, contact mode AFM images were collected using nonconductive silicon nitride probes (tip radius of 10 nm, DNP-S10, Bruker) at a scan rate of 0.999 Hz and deflection setpoint of 1.975 V. The scan area was 50 μm by 50 μm. Nanoscope software (Ver. 7.20) was used to analyze the images. Root mean square roughness ($R_q$) indicated the roughness values over the 50 μm by 50 μm areas. For each sample, at least four locations on the sample surface were measured to determine the roughness. The depth of the cracks in sample surfaces were also measured from the AFM images by taking the average of 20 spots from four representative AFM images.

Reacted biotite powders were measured for ζ potential by dynamic light scattering (Malvern, Zetasizer, nano series). To fully remove salts in the powders, the reacted biotite powders were mixed with 40 mL DI water and centrifuged for 15 min. This process was
repeated 10 times. Then the washed biotite powders were sonicated and dispersed in DI water. After 10 min of settling, the supernatant of the dilute fine particle suspension was measured for ζ potential. Using this procedure, because we removed salt and made identical measurement solutions for all samples, we obtained the net changes of biotite surface charge after reaction in different salinity solutions. The measurements were not influenced by the water chemistries, such as pH and ionic strength, of different reaction solutions.

After zeta potential measurements, the reacted biotite powders were oven-dried overnight. X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, Ulvac-PHI with monochromatic Al Kα radiation (1486.6 eV)) was used to investigate the surface functional groups of oxygen on biotite. The C 1s (284.8 eV) spectrum was taken as the energy reference. Narrow scans of O 1s spectra were analyzed with Shirley background subtraction. The pass energy for the narrow scans was 23.5 eV. The fitting of O 1s photolines were conducted based on the Gaussian-Lorentzian algorithm. The fitting was conducted using Multipak V 7.0.1 (Ulvac-PHI, Inc.).

2.3 Results and Discussion

2.3.1 Higher Salinity Enhances Biotite Dissolution

Biotite dissolution was significantly enhanced with increasing salinities. Figure 2.3 shows the released concentrations of interlayer K and the framework cations Si, Al, Fe, and Mg after biotite flake (Figure 2.3A) and powder (Figure 2.3B) dissolution for 70 h in DI water (i.e., 0 M NaCl) and 0.1, 0.5, and 1.0 M NaCl solutions at 102 atm of CO₂ and 95 °C. Ion-exchange reactions between interlayer K in biotite and Na⁺ in the solution were
promoted at higher salinities, leading to higher concentrations of K released into the solutions. Higher salinity also enhanced the release of framework cations.

The surface morphology was altered by salinity as observed in AFM analyses of biotite basal surfaces (Figure 2.4). After reaction in DI water for 70 h, the basal surface of biotite was still smooth and almost unaltered (Figure 2.4A). With higher salinities, deeper and more abundant cracks formed on the biotite basal surfaces, with crack depths of 4.2 ± 1.3, 7.8 ± 2.4, and 56.0 ± 8.4 nm for 0.1 M, 0.5 M, and 1.0 M NaCl samples, respectively. This trend was consistent with more significant ion-exchange reactions of aqueous Na⁺ and interlayer K in biotite at higher salinities, which was reported to contribute to crack formation.⁶⁵ Formation of cracks on biotite basal surfaces exposed edge sites, further enhancing basal surface alteration (Figure 2.4D). More pronounced formations of cracks increased the surface roughness (Rₙ) from ~1.5 to 16.6 nm (Figure 2.4). For all cases, secondary mineral formations were not significant, except for a very limited quantity of precipitates characterized as amorphous silica and fibrous illite, as reported in our previous study.⁶⁵ Thus, the effects of secondary precipitation on roughness changes could be ignored in this study.
In addition to morphology changes, dissolution also changed biotite’s surface charge. ζ potential measurements (Table 2.2) show a higher negative charge on biotite powder after reaction at higher salinities, with −19.1 mV for samples reacted in DI water and −47.6 mV for samples reacted in the 1.0 M NaCl solution. As reported by Bray et al., the release of interlayer K is not charge-conservative. More significant ion-exchange reactions occurred at higher salinities, and a larger amount of interlayer K leached into solutions (Figure 2.3B), resulting in a relative negative charge in the biotite near-surface after reactions.
AFM Images

A. DI water  B. 0.1 M NaCl  C. 0.5 M NaCl  D. 1.0 M NaCl

Rq: 1.5 ± 0.2 nm  Rq: 2.9 ± 0.7 nm  Rq: 5.6 ± 0.2 nm  Rq: 16.6 ± 1.3 nm

Static Contact Angles

40.6 ± 2.6 °  32.6 ± 0.8 °  23.7 ± 1.8 °  21.0 ± 2.4 °

Figure 2.4 AFM images of biotite basal planes after reaction for 70 h in DI water (A), 0.1 M NaCl (B), 0.5 M NaCl (C), and 1.0 M NaCl (D) solutions at 102 atm of CO2 and 95 °C. The height scale is 60 nm. Rq is the root mean square roughness of the corresponding samples. Static CAs were measured at 102 atm of CO2 and 48 °C in 0.1 M NaCl brine for the prereacted biotite flakes as in the top AFM images. Each data point represents the average value of 10 repeated measurements of the CO2 droplet on biotite basal surfaces. The error bar stands for the standard deviation of the measurements.

Table 2.1 Zeta potential measurements of biotite after reaction with different salinities.

<table>
<thead>
<tr>
<th>Surface charge (mV)</th>
<th>DI water</th>
<th>0.1 M NaCl</th>
<th>0.5 M NaCl</th>
<th>1.0 M NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-19.1±0.4</td>
<td>-36.3±1.1</td>
<td>-41.8±1.9</td>
<td>-47.6±1.5</td>
</tr>
</tbody>
</table>

2.3.2 Chemical Reactions Make Biotite Surfaces More Hydrophilic

To understand how chemical reactions affect biotite’s wettability, we measured high-temperature and high-pressure CAs for the prereacted biotite flakes. The static CAs of biotite basal surfaces decreased with increasing salinity (Figure 2.4). Previous studies indicated the presence of thin water films on mineral surfaces when scCO2 is injected into
deep subsurface reservoirs.\textsuperscript{56, 58, 75, 83-85} If a mineral surface can sustain thicker water films, it becomes more hydrophilic. To explain the static CA changes and their relationship to water film thickness, three possible mechanisms can be considered.

First, a reaction-induced roughness increase can decrease the CAs. Surface roughness is a crucial factor impacting surface wettability.\textsuperscript{63, 86-89} As indicated by the Wenzel relation, a hydrophilic solid becomes more hydrophilic when the surface roughness is increased.\textsuperscript{90} Rougher surfaces can support and stabilize thicker water films through both adsorption and capillarity.\textsuperscript{91-93} Compared with those of smooth surfaces, the capillary features of rough surfaces retain the wetting phase better because they can contain more mass in deeper channels. As shown in Figure 2.4 in our experiments, the biotite surface roughness increased from 1.5 ± 0.2 to 16.6 ± 1.3 nm after high-temperature and high-pressure reactions in DI water and 1.0 M NaCl solutions, respectively. Biotite is a hydrophilic mineral,\textsuperscript{94} and a rougher biotite surface could, thus, form thicker water films, with consequently decreased CAs and enhanced wettability.

Second, reaction-induced changes in surface charge can result in CA change. The surface charge can affect water film stability and thickness, with higher magnitude values supporting thicker films and being important in surface and interface phenomena such as wetting and adhesion.\textsuperscript{6} Tokunaga estimated the thickness of water films by considering van der Waals and electric double-layer interactions and found that a decreased surface charge of silica can result in a thinner electric double layer and in substantially thinner adsorbed water films.\textsuperscript{6} Similarly, we postulate that the more negatively charged biotite surface due to significant loss of K after reaction at higher salinity (e.g., −19.1 mV in DI and −47.6 mV in 1.0 M NaCl) can support thicker water films, making the surface more hydrophilic.
Hence, smaller CAs were observed for biotite samples after reaction at increasing salinities. A caveat was raised concerning the use of the $\zeta$ potential measurements of biotite powders in assessing the effect of surface charge on basal surface wettability. Powders have more reactive edge surfaces, and the $\zeta$ potential measured is more likely to be from edge surfaces. However, although the extents of the basal and edge surface charge changes might be different, the general trend is expected to be the same for the following reasons: First, basal surfaces and edge surfaces were reacted at the same time. Second, the formation of cracks (Figure 2.4) exposed edges on biotite basal surfaces that could also contribute to the changes in basal surface charges.

**Table 2.3** Percentage of biotite surface species of oxygen after reaction at different conditions.

<table>
<thead>
<tr>
<th></th>
<th>$\text{O}^2-$ (%)</th>
<th>OH (%)</th>
<th>H$_2$O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted</td>
<td>8.35</td>
<td>82.90</td>
<td>8.75</td>
</tr>
<tr>
<td>DI</td>
<td>8.60</td>
<td>82.93</td>
<td>8.47</td>
</tr>
<tr>
<td>0.1 M NaCl</td>
<td>7.69</td>
<td>86.05</td>
<td>6.56</td>
</tr>
<tr>
<td>0.5 M NaCl</td>
<td>3.95</td>
<td>89.21</td>
<td>6.84</td>
</tr>
<tr>
<td>1.0 M NaCl</td>
<td>1.58</td>
<td>92.86</td>
<td>5.56</td>
</tr>
</tbody>
</table>

Third, surface functional groups interact with the aqueous phase and affect its adsorption to mineral surfaces. Both bridging oxygens (T–O–T, T denotes a tetrahedral site) and terminal oxygens (T–OH) are present on the surface of aluminosilicates. The hydroxyl groups can undergo donor–acceptor interactions with H$_2$O and make hydrogen bonds; thus a higher density of hydroxyl groups makes a surface more hydrophilic. In general, breaking of T–O–T linkages is the key step in the dissolution of framework cations in aluminosilicates, and terminal oxygens form. We hypothesize that dissolution
reactions increase the amount of hydroxyl groups, thus making the biotite surface more hydrophilic. From XPS results (2-S3 and Table 2.3), we observed an increase in the level of hydroxyl groups from around 82.9% (DI) to 92.9% (1.0 M NaCl) on biotite surfaces that reacted at higher salinities. Stronger interactions were expected between water molecules and the biotite surfaces reacted at a higher salinity, leading to more hydrophilic surfaces. Therefore, changes in surface functional groups can also be a mechanism for the increasing hydrophilicity of biotite surfaces.

In summary, reaction-induced roughness, changes in surface charge, and changes in surface functional groups can affect simultaneously and contribute to the more hydrophilic biotite surfaces. Compared to the inconsistency in contact angle values of mica minerals summarized by Iglauer et al.,\textsuperscript{55} we suggest that the large uncertainties could come from the different chemical reaction extents of minerals during measurement.

2.3.3 Reacted Biotite Surfaces Exhibit a Lower CO\textsubscript{2} Adhesion and Contact Angle Hysteresis

Figure 2.5 shows representative images captured from dynamic CA measurements indicating CO\textsubscript{2} advancing (water receding) and CO\textsubscript{2} receding (water advancing) processes, and the corresponding contact angle hysteresis (CAH) values. The CAH is generally expressed as the difference between the advancing and receding water CAs. A more detailed explanation can be found section 2-S4 in the Supporting Information for Chapter 2. CO\textsubscript{2} adhesion refers to the event when the CO\textsubscript{2} droplet detached from the needle tip and remained attached to the biotite surface when the droplet was retracted by the pump. CO\textsubscript{2} adhesion was observed for all the biotite samples. However, CO\textsubscript{2} nonadhesion was also
observed on the biotite samples that reacted with 1.0 M NaCl solution. CO₂ adhesion indicates the atomic attractive forces between the contacted surfaces of the scCO₂ droplet and the biotite basal surface. The effect of surface roughness on adhesion has been studied, and a decrease in adhesion force with increasing surface roughness was reported. Thus, the adhesion force was expected to be lower between scCO₂ and biotite surfaces with a higher roughness after reaction with 1.0 M NaCl solution, reducing the incidence of CO₂ adhesion.

**A. Dynamic CA measurement process**

<table>
<thead>
<tr>
<th>CO₂ adhesion</th>
<th>CO₂ advancing</th>
<th>CO₂ receding</th>
<th>CO₂ adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Image]</td>
<td>[Image]</td>
<td>[Image]</td>
<td>[Image]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CO₂ non-adhesion</th>
<th>CO₂ advancing</th>
<th>CO₂ receding</th>
<th>CO₂ adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Image]</td>
<td>[Image]</td>
<td>[Image]</td>
<td>[Image]</td>
</tr>
</tbody>
</table>

**B. Summary of dynamic CA results**

<table>
<thead>
<tr>
<th>Experimental Condition</th>
<th>Adhesion</th>
<th>CAH (Left)</th>
<th>CAH (Right)</th>
<th>Contact line (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted</td>
<td>No</td>
<td>31.0</td>
<td>29.8</td>
<td>0.71</td>
</tr>
<tr>
<td>DI water</td>
<td>Yes</td>
<td>64.1</td>
<td>52.4</td>
<td>3.30</td>
</tr>
<tr>
<td>0.1M</td>
<td>Yes</td>
<td>53.3</td>
<td>52.9</td>
<td>1.24</td>
</tr>
<tr>
<td>0.5M</td>
<td>Yes</td>
<td>66.3</td>
<td>59.1</td>
<td>2.70</td>
</tr>
<tr>
<td>1.0M</td>
<td>~50% Yes</td>
<td>44.9</td>
<td>37.6</td>
<td>1.39</td>
</tr>
<tr>
<td>1.0M</td>
<td>No</td>
<td>42.7</td>
<td>40.9</td>
<td>0.76</td>
</tr>
</tbody>
</table>

**Figure 2.5** Dynamic CA measurements of biotite samples after reaction for 70 h in different salinities (0, 0.1, 0.5, and 1.0 M NaCl) at 102 atm of CO₂ and 95 °C. The CAs were measured in brine with 0.1 M NaCl, at 102 atm of CO₂ and 48 °C. (A) These images show CO₂ advancing (brine receding), CO₂ receding (brine advancing), and CO₂ adhesion or nonadhesion on biotite basal surfaces. (B) This table summarizes the dynamic CA measurement results.
The CAH also plays an important role in residual CO$_2$ trapping, including drainage and imbibition processes.$^{56, 103}$ During the drainage process, the brine is being displaced, and thus, the water receding CA is representative of this process. Conversely, during the imbibition process, the water advancing CA is operative.$^{56}$ Figure 2.5 shows larger CAH for those biotite samples for which CO$_2$ adhesion was observed. The contact line is the ternary phase line among biotite, CO$_2$, and brine. The length of the contact line at the last moment of the CO$_2$ receding process, and before CO$_2$ detached from the needle, is shown in Figure 2.5B. For CO$_2$ adhesion samples, the contact line was pinned (or stuck) to the biotite surface and did not move smoothly. The CO$_2$ droplet detached abruptly from the tip of the needle, leading to longer contact lines. After detachment, the CO$_2$ droplet adhered to the biotite surface. Hong et al.$^{104}$ suggested that in the captive drop method, the defect model, in which the contact angle hysteresis originates from a chemical defect that is more wettable than the rest of the surface, can successfully explain receding pinning of a sessile drop (water receding). They explained that during the captive drop method, when the liquid phase retreat is driven by an inflating CO$_2$ bubble, a defect located in the liquid phase is unable to pin the contact line. As a result, the defect model fails to describe continuous retreat of the liquid phase driven by an inflating bubble and water advancing pinning during CO$_2$ receding associated with a captive droplet. Using adhesion hysteresis, in which the dissipation of energy during advancing and receding are dominant instead of a hypothesized more wettable defect, they showed that contact line pinning associated with liquid advancing can be explained by free energy minimization and contact line pinning is a result of contact angle hysteresis. This suggestion can also explain our finding that CO$_2$ adhesion contributed to larger CAH and to longer contact line on mineral surfaces.$^{105}$
2.4 Environmental Implications

Salinities promote biotite dissolution by enhancing ion-exchange reactions, resulting in larger surface roughness, more negative surface charges, and higher densities of surface hydroxyl groups, which subsequently impact biotite wettability under GCS relevant conditions. This information has important implications for capillary trapping and stratigraphic trapping of CO₂ in GCS sites. In subsurface sites, the pores are occupied by brine. After scCO₂ is injected, it can enter the pore throats, displacing brine (drainage). When the injection pumps stop, the brine re-enters the pores (imbibition), leaving some CO₂ trapped in the pore spaces by capillary forces that is determined by wettability. Moreover, scCO₂ may dissolve in brine. The acidified brine can flow into the pores and react with the minerals. Once chemical reactions between scCO₂ or acidified brine and minerals cause wettability changes of pores, the increased hydrophilicity leads to higher capillary pressure. In other words, it becomes more difficult for CO₂ to diffuse and be transported through porous formations, which is beneficial for the residual trapping of CO₂ and sealing of the caprocks. However, there are other factors influencing capillary pressure, such as pore size. Mineral dissolution can increase the pore size, decreasing the capillary pressure. On the other hand, precipitation can decrease pore size, resulting in the opposite effect. Therefore, property changes of minerals induced by reactions are complicated and should be considered carefully.

During the imbibition process, adhesion of CO₂ droplets onto mineral surfaces can immobilize CO₂ and increase the level of CO₂ residual trapping. Larger CAH leading to more significant CO₂ contact line pinning will also inhibit CO₂ movement. Moreover, in CO₂-enhanced oil or gas recovery, CO₂ flooding is used to drive oil movement and promote
oil production. On the one hand, inhibition of CO₂ movement may decrease the oil displacement efficiency. On the other hand, it may also prevent the bypass flow of scCO₂ and thus increase oil recovery. Furthermore, CAH affects the saturation hysteresis during residual CO₂ trapping, and this information can aid numerical models that include hysteresis in predicting the CO₂ distribution because drainage and imbibition cycles occur during GCS.¹⁰⁸⁻¹⁰⁹ There is, however, a caveat that adhesion occurring in laboratory scale experiments can be different from the translation of a meniscus during displacement processes in the pore space of rocks. Future systematic scale-up studies should improve our understanding of CO₂ adhesion.

Although other mica group minerals differ in elemental composition from biotite and can be less reactive, they share similar subunit structures, containing interlayer, tetrahedral, and octahedral sheets and having perfect cleavage along the {001} basal planes. If these mica group minerals undergo reactions under GCS conditions, the effect of these reactions on wettability can therefore be similar. Thus, a better understanding of the effects of salinity on biotite can help predict the general dissolution trend of other abundant mica group minerals in shales. Additionally, chemical reaction-induced surface changes significantly affect wettability. On the basis of the results of this study, we can also infer that if the chemical reactions triggered smoother surfaces that had fewer surface charges or contained fewer surface hydroxyl groups, there could be a decrease in the hydrophilicity of minerals. Here, for the first time, we experimentally related salinity-induced chemical reactions to the wettability changes of minerals under GCS conditions. Our findings elucidate the relationships among salinity, chemical reactions, and wettability changes of
minerals under conditions relevant to energy-related subsurface operations, thus benefiting GCS and oil and gas recovery.

Acknowledgments

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Supporting Information for Chapter 2

2-S1. Model mineral

Micas, an abundant group of minerals in the caprocks of subsurface formations, have perfect cleavage along the {001} basal plane, and are widely used in wettability studies. Biotite, which is a reactive mica mineral, and its weathering product, glauconite, have been reported to be present in several energy-related subsurface operation sites. At GCS sites, faults and cracks were reported in low-permeability caprocks where mica existed, which can potentially expose biotite surfaces. In this study, biotite was chosen as the model mica mineral. Additionally, previous studies have indicated the alteration of biotite surface morphology and formation of secondary minerals on biotite basal surfaces under GCS conditions, which can lead to wettability changes. Although other mica minerals can be less reactive than biotite, because the time scale of CO₂ storage is much longer than our reaction time (70 h), mica minerals can slowly react and result in wettability alteration. In other words, as long as the reaction occurs while the reaction kinetics can be different with different mica minerals, the influence on wettability can be generalized. Furthermore, while reactive interfaces at field sites may contain a mixture of different minerals with various geometries, examining the effects of salinity-induced chemical reactions on biotite wettability alteration can be a good starting point towards a better understanding of the interplay of chemical reactions and wettability alteration.

2-S2. High temperature and high pressure contact angle measurement setup

The captive drop method was used to measure contact angles on pretreated biotite basal surfaces with a high pressure and temperature contact angle (CA) measurement chamber (Temco, IFT-10), as used in previous work by Jung and Wan. Figure 2.2 shows the apparatus. The chamber was placed in a glovebox to maintain its temperature. A biotite flake was horizontally mounted to the stainless-steel plate by two stainless clips. CO₂ was first introduced into the chamber and pressurized to 102 atm. The chamber was heated by
surrounding heating tapes, and CO$_2$ was allowed to equilibrate for about 1 h. The temperature of the entire glove box was maintained at a constant temperature of 48±1 °C during the experiments. The temperature and pressure during measurements were chosen according to the geologic depth relationship of temperature and pressure, and were representative of conditions at about 1 km depth. Moreover, the temperature was lower than the reaction temperature (95 °C) to slow down biotite dissolution and avoid unwanted reactions during CA measurements. Because all samples were prepared at the same temperature and pressure, the temperature history did not cause significant difference between samples. After equilibrium, 0.1 M NaCl solution, saturated with 102 atm CO$_2$ at 48 °C overnight, was injected into the chamber to displace supercritical CO$_2$ (scCO$_2$) and stabilized for about 30 min. Different from most previous wettability studies, in our study, biotite samples were reacted in specific salinities for 70 h before CA measurements. Then, the CAs were all measured in 0.1 M NaCl solution. Therefore, the influence of salinity on CA during its measurement could be ignored. We focused on investigating the effects of salinity-induced chemical reactions on biotite wettability alteration, not the direct effects of salinity.

For static CA measurements, a scCO$_2$ droplet was formed at the tip of the needle inside the brine-filled chamber and released onto the biotite basal surface above it. The images of the droplet on biotite surface were recorded with high-resolution time-lapse photography (6.2 Megapixel, Nikon D7000). Ten measurements were taken of the same biotite samples. For dynamic CA measurements, a scCO$_2$ droplet was generated at the tip of the needle, which was adjusted to be closer to biotite basal surface than for static CA measurements. The scCO$_2$ droplet was contacted with the biotite basal surface while the needle tip was still immersed in the droplet. By injecting and withdrawing scCO$_2$, controlled by a syringe pump connected to the needle, the droplet was slowly expanded and contracted on the biotite surface. Five to eight dynamic CA measurements were made for each sample, and videos were recorded by the camera. It took about 5 hours for CA measurement on every sample, which was shorter than the pretreatment time (70 h). Therefore, there was not enough time for significant chemical reactions to occur. When the entire measurement was done, the solution in the chamber was collected and measured by ICP-OES. The results are shown in Table 2-S1. The released cation concentrations were
much lower than those released during pretreatment reactions at 95 °C (Figure 2.3). We also reacted biotite in 0.1 M solution at 48 °C and 102 atm CO$_2$ for 5 h and compared the surface morphology of the reacted biotite with unreacted biotite, using AFM. The AFM images (Figure 2-S1) confirmed that there is no discernible alteration of biotite basal surfaces. Therefore, we can conclude that even though minor reactions may occur during CA measurements, these are expected to be the same reactions as in pretreatment, but to a lower degree. We do not believe they cause significant changes of surface chemistry.

Table 2-S1 Released ion concentrations from biotite after contact angle measurements (unit: µM).

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>18.90</td>
<td>7.12</td>
<td>15.04</td>
<td>2.88</td>
</tr>
<tr>
<td>0.1 M</td>
<td>24.83</td>
<td>7.12</td>
<td>123.92</td>
<td>3.29</td>
</tr>
<tr>
<td>0.5 M</td>
<td>26.31</td>
<td>12.82</td>
<td>59.63</td>
<td>7.41</td>
</tr>
<tr>
<td>1.0 M</td>
<td>24.09</td>
<td>17.45</td>
<td>40.11</td>
<td>12.76</td>
</tr>
</tbody>
</table>

Figure 2-S1 AFM images of unreacted biotite basal planes (A), reacted biotite in 0.1 M NaCl solution at P$_{CO_2}$ = 102 atm and T = 48 °C for 5 h. The height scale is 80 nm.

After the images were obtained, ImageJ software, combined with DropSnake and Low-Bond Axisymmetric Drop Shape Analysis (LB-ADSA) plugins, was used to analyze the CAs. As a convention, the CA values reported hereinafter refer to the water phase. The lowest and highest CA values from images captured in the video of dynamic CA
measurements were reported as the receding ($\theta_R$) and advancing ($\theta_A$) CAs, respectively. The length of the contact line was measured from the CO$_2$ receding images.

2-S3. Characterization surface functional groups

Both bridging oxygens (T–O–T, T: tetrahedral site) and terminal oxygens (T–OH) are present on the surface of aluminosilicates.$^{95-96}$ Water molecules are also on the mineral surface. By deconvolution of the oxygen peak in the range of 528-536 eV observed in our XPS measurements (Figure 2-S2) into the three species, the peak with binding energy of 530.5 ± 0.1 eV was assigned to bridging oxygen (O$^2$), the peak with binding energy of 531.6 ± 0.1 eV was assigned to hydroxyl oxygen (–OH), and the peak with binding energy of 533.2 ± 0.1 eV was assigned to water molecules (H$_2$O), according to the literature.$^{110-111}$ Next, the percentages of oxygen species at the biotite surface after reaction at different salinities at 95 °C and 102 atm CO$_2$ were obtained, and are shown in Table 2.3. The percentage of hydroxyl group increased from 82.90% to 92.86% after reaction with 1.0 M NaCl solution.

Figure 2-S2 Example of the deconvolution of the oxygen peak.
2-S4. Contact angle hysteresis (CAH)

As described in 2-S2, dynamic contact angle measurements were conducted using the captive drop method. Water phase retreat was driven by inflating the CO\(_2\) bubble. When the volume of the CO\(_2\) bubble was increasing (CO\(_2\) advancing), the water phase was retreating (water receding). By the same token, when CO\(_2\) was receding, the water phase was advancing. During CO\(_2\) advancing, when the highest CO\(_2\) contact angle was reached, the water contact angle (180°-CO\(_2\) contact angle) was reported as the receding contact angle. During CO\(_2\) receding, at the lowest CO\(_2\) contact angle, the water contact angle was reported as advancing contact angle. The contact angle hysteresis value is generally expressed as the difference between the advancing and receding contact angles.

2-S5. Dissolution stoichiometry

Figure 2.3 shows the total released cation concentrations from flake and powder dissolutions, which are not normalized by surface area. The trends of increasing release of K at higher salinity were similar for both cases. This is reasonable because the release of K is through ion-exchange reactions. The total surface area for powders was larger than for flakes, so the total released K concentrations were higher for powders than flakes. As for the release of framework cations, the edge sites are more reactive than basal surfaces. Powders have larger surface areas as well as higher percentage of exposed edge surfaces. Hence, the concentrations of released framework cations from powders were also higher than from flakes. Regarding stoichiometry, for both flake and powder dissolution, loss of K was obviously preferential than frameworks cations. For flake dissolution, the release of Al was preferred over other framework cations at 1.0 M NaCl solution, while the dissolutions for framework cations were congruent at lower salinities. For powder dissolution, since there were fine biotite particles remaining on the sieved powders (53–106 µm), they dissolved much faster than larger particles. There were no general trends in the stoichiometry of framework cation dissolutions from powders.
2-S6. Comparison to previous studies

Previous studies mainly investigated the direct effects of salinity on wettability caused by interfacial tension. They rarely focused on the effects of chemical reactions and the resulting surface property changes on wettability alteration. Our contribution in this study is that for the first time, we experimentally related salinity-induced chemical reactions to the wettability changes of minerals under GCS conditions. In this study, we clearly linked wettability and the changes of surface properties, such as roughness, surface charge, and surface functional groups, induced by chemical reactions. Further, we applied the theories to discuss the wettability changes. Our study will fill the urgent need to understand the unexplored relationships among salinity, chemical reactions, and
wettability changes of minerals. As Iglauer reported,\textsuperscript{55} there are considerable uncertainties regarding wettability studies including for mica minerals. There are differences between our study and those studies on mica minerals included in Iglauer’s review. Our observed contact angle values fall in the wide range of contact angle values (12\textdegree{}–50\textdegree{}) of mica included in that review. Their studies investigated the influence of salinity on contact angle, and their contact angles were measured under different salinity conditions. However, we pre-reacted the biotite surfaces under different salinities for 70 h and the contact angles were measured under the same salinity (0.1 M NaCl). The influence of salinity on contact angles during measurement could thus be ignored, and we could focus on the effects of chemical reaction-induced surface property changes on wettability. The differences between our study and those in Iglauer’s review and the inconsistency on contact angle values of mica minerals might come from the chemical reactions occurred.

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Abstract

High concentrations of organics are reported in deep saline aquifers, and among them, carboxylic anions are a major constituent that can affect the geochemical reactions of minerals. In this chapter, in addition to the investigation on the impact of salinity in Chapter 2, we study the effects of two representative organic oxyanions (acetate and oxalate) with small molecular weights on biotite’s dissolution and surface morphological changes. The experimental conditions were chosen to be relevant to GCS sites (95 °C and 102 atm CO₂). Quantitative analyses of dissolution differences between biotite edge and basal planes were made. Acetate slightly inhibited biotite dissolution and promoted secondary precipitation. The effect of acetate was mainly pH-induced aqueous acetate speciation and the subsequent surface adsorption. Under the experimental conditions, most of acetate exists as acetic acid and adsorbs to biotite surface Si and Al sites, thereby reducing their release. However, oxalate strongly enhanced biotite dissolution and induced
faster and more significant surface morphology changes by forming bidentate mononuclear surface complexes. For the first time, we show that oxalate selectively attacks edge surface sites and enhances biotite dissolution. Thus, oxalate increases the relative reactivity ratio of biotite edge surfaces to basal surfaces, while acetate does not impact this relative reactivity. This study provides new information on reactivity differences at biotite edge and basal planes in the presence of organic ligands, which has implications for safe CO$_2$ storage in organic-rich sites.

3.1 Introduction

To reduce anthropogenic CO$_2$ emission to the atmosphere, geologic CO$_2$ sequestration (GCS), as well as combined supercritical CO$_2$-enhanced oil recovery (CO$_2$-EOR), has received increasing attention as a promising strategy.$^{1,112-114}$ Experimental and modeling studies have reported that geochemical reactions between scCO$_2$-saturated brine and preexisting rocks may change the porosity, permeability, and wettability of the preexisting rocks.$^{38-43,115-117}$ For example, Shiraki et al. conducted core-flooding laboratory experiments to study water–rock interactions during CO$_2$ flooding in the Tensleep Formation, Wyoming, USA. They reported permeability decreases of the cores because of kaolinite crystal growth in pore throats, despite dissolution.$^{41}$ In terms of wettability, Chiquet et al. reported a transition for mica and quartz from a water-wet behavior at low CO$_2$ pressure toward an intermediate wettability at high pressure, and the wettability alteration was more pronounced in the case of mica than quartz.$^{38}$ Porosity, permeability, and wettability are important properties affecting CO$_2$ trapping mechanisms and the fate and transport of CO$_2$. Therefore, for the safety and efficiency of the GCS process, the
interactions between scCO$_2$-saturated brine and preexisting rocks, and the subsequent property changes of rocks, should be studied carefully.

 Many studies have reported that there are abundant organics, such as kerogen, carboxylic acids, and BTEX (benzene, toluene, ethyl-benzene, xylene), in deep saline aquifers and current GCS sites.$^{26, 118-122}$ The total organic concentrations are in the range of 5–10000 mg/L, and among them, short-chain carboxylic acid anions are one main group. Field data and laboratory experimental data demonstrated that thermal alteration of kerogen in shales is the dominant process to produce aqueous organic acid anions in basins.$^{119, 121, 123}$ Additionally, after the injection of CO$_2$, mobilization of organic compounds (mainly formate and acetate) from reservoir rock was reported in the on-shore CO$_2$ storage site at Ketzin (Germany).$^{124}$ In oil and gas reservoirs, which can potentially be used as CO$_2$-EOR sites, the concentrations of organics can be even higher than in deep saline aquifers.$^{119, 125-126}$ The complexing organic ligands can affect water–rock interactions by buffering the pH of the system$^{127-128}$ or by affecting the kinetics and reaction mechanisms of mineral dissolution by complexing with cations in the solution$^{129-131}$ or on surface sites of minerals.$^{132-133}$

 Under ambient conditions, the effects of organic ligands on the dissolution of aluminum silicates, feldspars, and mica have been studied.$^{130, 132, 134-136}$ For example, according to Suarez et al.$^{132}$ and Stumm et al.$^{136}$ oxalate ion forms bidentate mononuclear complexes with alumino-site on anorthite (CaAl$_2$Si$_2$O$_8$) or kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) surfaces, thus promoting their dissolution. However, under GCS conditions at elevated temperatures and pressures and high salinities, there are only a few reported works, but the effects of organic ligands are likely to be different from those under ambient conditions.$^{67}$
Yang et al. reported that acetate inhibited anorthite dissolution and increased secondary mineral precipitation, and the effect of acetate was more significant in systems with lower salinity and lower pH under GCS conditions. They also found that scCO$_2$ in the experimental systems caused anomalous plagioclase dissolution behaviors compared to results from a high pressure N$_2$ and low pH condition. Shao et al. investigated the effects of organic ligands (oxalate, malonate, acetate, and propionate) on scCO$_2$-induced phlogopite dissolution and secondary mineral formation, finding increased phlogopite dissolution rates in the presence of chelating agents. As recently reported, the presence of organic ligands may enhance or inhibit mineral dissolutions and secondary precipitations in GCS sites, which will affect CO$_2$ trapping mechanisms and change the storage capacity of reservoirs. Ultimately, we need an improved understanding of the extent to which different organic ligands impact the minerals and of the mechanisms by which they induce related reactions under GCS conditions.

Among minerals abundant in caprocks in GCS sites, this study focused on micas, which were reported with a mass fraction of about 30% in the Sleipner shales in Norway and 10–33% in the Venture gas field in Canada. Biotite, a mica with the chemical formula K(Mg,Fe)$_3$(Si$_3$O$_{10}$)(F,OH)$_2$, was chosen as a model mineral because a weathered form of biotite, glauconite, was reported in geological seals considered for saline CO$_2$ sequestration in the Gulf Coast and Illinois Basin, and biotite contains reactive Fe as the framework ions. Biotite has an anisotropic structure with a perfect cleavage along the {001} basal planes. From previous observations, the edge surfaces of phyllosilicates are 40 to 200 times more reactive than the basal surfaces, thus dissolution preferentially happens on crystal edges. The dissolution rates of minerals generally depend
on the mineral surface area. Most mineral dissolution rates are thus reported after normalization by the mineral surface area.\textsuperscript{98} Because the reactive surface area is not the same as the total surface area for phyllosilicates, structural anisotropy should be considered when interpreting the dissolution rates of phyllosilicates as well as the effects of organic ligands on dissolution of phyllosilicates. However, under GCS relevant conditions, previous studies rarely considered anisotropic dissolution.\textsuperscript{65, 137} Moreover, in organic-containing systems, the relative reactivity of edge and basal surfaces is little known. We hypothesized that preferential attack by organic compounds on specific mineral planes might result in preferential dissolution and secondary mineral formation of particular planes. Therefore, when evaluating potential sites for CO\textsubscript{2} sequestration, both the existence of organic ligands and the compositions of preexisting rocks should be taken into account.

We still have significant knowledge gaps on the effects of organic ligands on biotite dissolution under GCS conditions, especially anisotropic dissolution, and on secondary precipitation. In this study, acetate and oxalate were chosen as model carboxylic acids as a first step to study the roles of organic ligands. Hence, the objectives of this study were first to investigate the overall effects of acetate and oxalate on scCO\textsubscript{2}-saturated brine–biotite interactions under GCS conditions (95 °C and 102 atm CO\textsubscript{2}). Second, by considering the pH effect of organic ligands and the structural anisotropy of biotite, we further explored the mechanisms of the effects of acetate and oxalate. Our findings will help understand how organic ligands affect biotite reactivities in GCS sites and will aid in evaluating caprock integrity during GCS and CO\textsubscript{2}-EOR operations.
3.2 Experimental Section

3.2.1 Chemicals and Mineral Sample Preparation

All solutions were prepared using at least ACS grade chemicals and deionized (DI) water (resistivity > 18.2 MΩ·cm, Barnstead Ultrapure water systems, Dubuque, IA). To simulate brine in deep saline aquifers, NaCl was added to adjust the background salinity of the solution to 1.0 M, based on reports from the GCS field sites. Organic ligands were added as sodium salts, and sodium acetate (EMD Millipore) and sodium oxalate (Alfa Aesar) were chosen as model organic ligands in this study. Diluted trace metal hydrochloric acid (HCl, BDH) and sodium hydroxide (NaOH, BDH) were used to adjust the initial pH of the system.

Biotite single crystals used in this study were acquired from Ward’s Natural Science, NY, and originated from Bancroft, Ontario, Canada. Biotite has a basic 2:1 layer structure composed of two opposing tetrahedral sheets with an octahedral sheet. The tetrahedral sheets are occupied by Si and Al, and the octahedral sheet is occupied by Fe and Mg. The charge balance is maintained by interlayer K. The chemical compositions of biotite samples were analyzed by X-ray fluorescence (XRF) and are shown in Table 2.1.

The chemical formula was determined to be $K_{0.91}Na_{0.08}Ca_{0.005}(Mg_{0.57}Mn_{0.02}Fe_{0.37}Ti_{0.04})_3(Al_{1.00}Si_{3.00})O_{10}(F_{0.51}(OH)_{0.49})_2$. Biotite flakes with a thickness of $80 \pm 10 \mu m$ were prepared by freshly cleaving specimens along the {001} basal planes and cutting them into $2.0 \text{ cm} \times 0.8 \text{ cm}$ rectangles. The biotite flakes were then washed with ethanol, acetone, and isopropanol to remove organic matter, and finally washed with DI water. To investigate biotite’s anisotropic dissolution, a set of
biotite flakes with different dimensions was prepared according to Figure 3.1. First, same size biotite flakes were prepared and, then, cut into two, three, and four smaller pieces. Thus, the four groups of biotite samples had the same sample mass, sample thickness, and surface area of basal planes, but varied surface areas of edge planes and perimeters.

![Figure 3.1 Sample preparation to investigate anisotropic dissolution of biotite.](image)

3.2.2 High Temperature and High Pressure Dissolution Experiments

High temperature and high pressure experiments were conducted in a benchtop reactor similar to that used in our group’s previous experiments (Figure 2.1). CO₂ was pressurized by a syringe pump (Teledyne Isco Inc., Lincoln, NE), introduced to the reactor (250 mL, Parr Instrument Co., IL) and maintained at 102 atm. The temperature of the reactor was controlled at 95 °C. The temperature and pressure were within the temperature and pressure ranges of GCS sites (31–110 °C, 73.8–600 atm). Although the experimental temperature and pressure conditions did not follow the depth relationship of temperature and pressure (T (°C) = 15 + 33 d and P (atm) = 1 + 100 d, where d is depth in kilometers), the relatively high temperature accelerated the reactions and
made experimental observations possible within reasonable time frames and were comparable with previous studies. Furthermore, Hu et al. found that under similar pressure conditions as in our experiments, the pressure did not affect biotite dissolution; therefore, while the pressure is lower than estimated pressures at the 2.42 km and 95 °C temperature conditions, the lower pressure did not significantly affect our experimental results.

Two initial concentrations of sodium acetate were used, 10 and 50 mM, and the sodium oxalate concentration was 10 mM. Acetic acid has been reported as the main short-chain carboxylic acids in brines. Although 10 mM oxalate is higher than the concentrations reported in subsurface sites, the concentrations of organic compounds can be higher after CO₂ injection due to extraction by scCO₂. For comparison, control experiments were conducted in 1.0 M NaCl solution without adding any organic ligands. For all experiments, to mimic pH condition under 95 °C and 102 atm CO₂, the initial pH of the system was adjusted to 3.16, which is the pH of the control system calculated by Geochemist’s Work Bench (GWB, Release 8.0, RockWare, Inc.).

Biotite flakes were placed in triplicated PTFE tubes containing 4 mL of prepared solutions and the tubes were put in the 250 mL reactor. The batches were stopped after reaction for the desired elapsed time, and the solutions were collected after filtering them through 0.2 µm polypropylene membrane and acidified in 1% trace metal nitric acid (HNO₃). The acidified samples were then analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). Ion chromatography (IC) was used to measure the residual organic concentration in the solution. The recovered biotite flakes were carefully
cleaned with DI water and dried using high purity nitrogen gas and, then, preserved for further characterizations of surface morphology.

To provide quantitative comparisons between edge surface and basal surface dissolutions, four groups of biotite flakes as described in Figure 3.1 were placed in four PTFE tubes, each containing 4 mL of prepared solutions. The sample collection process was the same as in the general experiments described above.

3.2.3 Analyses of Surface Morphological Changes

Atomic force microscopy (AFM, Nanoscope V Multimode SPS, Veeco) was used to analyze the surface morphology changes of biotite flakes after reaction. AFM height images were collected in contact mode under ambient conditions, with a scan rate of 0.999 Hz and deflection set point of 1.975 V. Nonconductive silicon nitride contact mode probes were used (tip radius of 10 nm, DNP-S10, Bruker). The cantilever was 206 μm long, without coating on the front side but with 45 ± 10 nm of Ti/Au coating on the back side. Height profile cuts on AFM height images, obtained using Nanoscope v7.20 software, provided information on the height of the precipitates and depth of the dissolution pits or dissolution channels.

3.2.4 Identification of Secondary Mineral Phases

To investigate the effects of acetate and oxalate on edge dissolution and secondary mineral formation on edge surfaces, additional batch experiments were conducted using 5 mm thick biotite specimens for 7 days. Samples were collected and then characterized by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX, Nova NanoSEM 230). The samples were coated with AuPd, and the electron accelerating voltage
during measurement was 10.00 kV. To characterize fibrous precipitates on basal surfaces, high resolution-transmission electron microscopy (HR-TEM, JEOL JEM-2100F field emission) was used. Reacted biotite flakes were sonicated in DI water to detach precipitates, and a droplet of the suspension was placed on a Formvar/carbon coated-Cu TEM grid (Electron Microscopy Science, PA) and measured. Electron diffraction patterns were obtained to identify the phase of the precipitates.

### 3.2.5 Fourier Transform Infrared (FTIR) Spectroscopy Analyses

To investigate the types of complexes between oxalate and biotite surface sites, attenuated total reflectance (ATR)-FTIR spectroscopy was used. The ATR-FTIR spectra were collected using a Thermo Scientific, Nicolet Nexus 470 spectrometer and a Smart Performer with a Ge crystal (Pike Technologies). Biotite powder with average size of about 100 nm was suspended in ethanol, deposited onto Ge crystal, and allowed to dry. Solutions of (a) 1 M NaCl and (b) 1 M NaCl + 10 mM Na$_2$C$_2$O$_4$ were prepared. The pH of the solutions was adjusted to 3.16, which is the same as the pH under conditions at 95 °C and 102 atm CO$_2$ with 1 M NaCl. The spectra were collected with 800 scans at a resolution of 2 cm$^{-1}$. 
3.3 Results

3.3.1 Enhanced Biotite Dissolution by Oxalate and Inhibited Dissolution by Acetate

The effects of oxalate and acetate on aqueous ion concentrations during biotite dissolution are shown in Figures 3.2 and 3.3. Aqueous K, Al, Si, Mg, and Fe concentrations in the systems were obtained at elapsed times of 3, 8, 22, 44, 70, and 96 h. The residual concentrations of organic ligands are shown in Figure 3-S1. Lower K concentrations were observed in the oxalate system (Figure 3.2) than in the control systems. In general, interlayer cations (K$^+$ in the case of biotite) are released by ion exchange reactions with H$^+$ and Na$^+$. The initial pH of the systems was adjusted to be same (pH = 3.16); however, the final pH values at 96 h were different between the control and organic-containing systems due to biotite dissolution, which were calculated by GWB (Table 3.1). The aqueous chemistries after 96 h reaction were employed in the calculations, and detailed information is provided in the Supporting Information for Chapter 3. In the presence of oxalate, the final pH (pH = 4.54; Table 3.1) was the highest of the control and organic-containing systems, leading to fewer ion exchange reactions with H$^+$ and, thus, lower concentrations of K. However, for the framework cations, such as Al, Si, Mg, and Fe, the presence of oxalate induced 5–10 times higher concentrations than those in control experiments. This finding suggests that oxalate significantly enhances the release of framework cations from biotite. The higher concentrations of framework cations in solution, in turn, contributed to the higher final pH in the oxalate system as well.
Figure 3.2 Aqueous concentrations of K, Al, Si, Fe, and Mg from dissolution of biotite at $P_{CO_2} = 102$ atm and $T = 95$ °C, with an ionic strength of 1.0 M and initial pH of 3.16. To distinguish the effects of organic ligands, control experiments were conducted at the same experimental temperature and pressure conditions but without adding organic ligands. Error bars are the standard deviation of triplicate experiments.

Figure 3.3 shows the evolution of aqueous ion concentrations for experiments with two different initial acetate concentrations (10 and 50 mM). Lower concentrations of framework cations were observed in the presence of acetate than in control experiments, indicating acetate’s inhibition effect on biotite dissolution. With 50 mM acetate, the released concentrations of tetrahedral framework cations Si and Al were 40 % lower than the ion concentrations with 10 mM acetate. Interestingly, for the octahedral cations, such
as Fe and Mg, different initial acetate concentrations produced only similar concentrations. We will further discuss the mechanisms in the Discussion section.

**Figure 3.3** Effect of acetate concentrations on aqueous ion concentrations of K, Al, Si, Fe, and Mg during dissolution of biotite at $P_{\text{CO}_2} = 102$ atm and $T = 95 \, ^\circ\text{C}$, with an ionic strength of 1.0 M and initial pH of 3.16. Acetate concentrations were 10 and 50 mM. Error bars are the standard deviation of triplicate experiments.

### 3.3.2 Effects of Acetate and Oxalate on Biotite’s Surface Morphological Changes

The evolution of the surface morphological changes due to biotite dissolution and secondary precipitation were clearly observed from AFM analyses of basal surfaces of the
reacted samples in the absence and presence of organic ligands (Figure 3.4). Two main features, fibrous precipitates and surface cracks, were observed on biotite surfaces, which agree with previous observations by Hu et al.\textsuperscript{65} The fibrous precipitates were identified to be fibrous illite, because of their measured d-spacings, fibrous shape, and the 120° intersection of the precipitates. They reported that the fibrous illite formed by oriented aggregation of small hexagonal nanoparticles and cracks formed due to ion-exchange reactions of aqueous Na\textsuperscript{+} with interlayer K\textsuperscript{+} in biotite and CO\textsubscript{2} intercalation. Furthermore, the cracked layers peeled off during biotite dissolution in brine at varied temperatures and CO\textsubscript{2} pressures in the absence of organic ligands.\textsuperscript{65-66, 78} Statistical analyses of the height of fibrous precipitates and depth of cracks were made by taking the average of 80 spots where fibrous precipitates or cracks were located in four representative AFM images (detailed information in 3-S2). In the presence of 10 mM acetate, the height (11.7 ± 2.1 nm in Figure 3.4A3 and 15.3 ± 2.2 nm in Figure 3.4B3) and amount of fibrous precipitates were promoted, which could also lead to lower aqueous ion concentrations of Al, Si, Mg, and Fe. Depth analyses (3-S2) indicated that the cracks were shallower in the presence of 10 mM acetate (~7.3 ± 1.5 nm, 22 h) than in control experiments (~16.1 ± 3.0 nm, 22 h). The results are consistent with the inhibited biotite dissolution and enhanced secondary precipitation by acetate.

With oxalate, even more prominent morphological changes were observed. Oxalate induced more extensive formation of secondary precipitates with a higher coverage of fibrous precipitates (Figure 3.4C1) on biotite basal planes than control (Figure 3.4A1) and acetate samples (Figure 3.4B1 and 3.4D1). Cracks were formed within 3 h reaction, much faster than those in the control and acetate systems after 22 h reaction. After 8 h reaction,
surface cracks connected to make bigger and deeper dissolution channels, and due to fast
dissolution and the formation of cracks, fibrous illites detached from basal surfaces and so
were less observable. The image in Figure 3.4C3 shows cracked biotite layers peeled from
basal surfaces, exposing fresh surfaces to the surrounding solution. After 44 h reaction with
oxalate (Figure 3.4C4), a fresh, new flat basal surface was exposed with shallow cracks.
Then precipitates again covered the surfaces after a longer time, making the shallow cracks
not observable (Figure 3.4C5 and 3.4C6 and supporting images in Figure 3-S4).

**Figure 3.4** Height mode AFM images of biotite basal planes after reaction in 1.0 M NaCl solution
at $P_{CO_2} = 102$ atm and $T = 95$ °C, with an ionic strength of 1.0 M and initial pH of 3.16, without
organic ligands (A), with 10 mM acetate (B), with 10 mM oxalate (C), and with 50 mM acetate
(D). The AFM images are 50 μm × 50 μm. The height scale is 60 nm for images A–D, but 100 nm
for C5 and 200 nm for C6. The different data scales show the results more clearly.
3.3.3 Biotite Anisotropic Dissolution

To further investigate the mechanisms of the effects of acetate and oxalate on biotite dissolution, we conducted experiments considering the structural anisotropy of biotite. Concentrations from dissolution experiments using four groups of biotite samples with different edge surface areas exposed (Figure 3.1) were fitted according to the following equation by a least-squares procedure, using Matlab (Mathworks, R2012b):

\[ C = r_E \text{ES} + r_B \text{BS} \]  

(3.1)

where \( C \) represents the ion concentration measured by ICP-OES, and ES and BS represent the apparent edge surface area and basal surface area, respectively. After fitting, the \( r_E \) value obtained indicates the edge surface area’s normalized dissolution contribution to the total ion concentrations released, and \( r_B \) indicates the dissolution contribution from basal surfaces. The \( r_E/r_B \) ratio can express the relative reactivities of edge surfaces and basal surfaces. Ratios of \( r_E/r_B > 1 \) were obtained for all three systems, which indicated that dissolution of biotite edge surfaces was preferred, and also preferred in the presence of acetate and oxalate (Figure 3.5). Our \( r_E/r_B \) ratio for control experiments was close to what Turpault reported,\(^21\) an \( r_E/r_B \) ratio of about 30, after biotite dissolution in diluted HNO\(_3\) solution (pH = 1.08 ± 0.02) under ambient conditions for 75 h. On the other hand, in our study, the extent of preferential dissolution of edge surfaces varied among the experiments, with or without organic ligands. Without any organic ligands, the \( r_E/r_B \) ratios increased with reaction time from 3 to 8 h but remained almost the same after 22 h (Figure 3.5A). Figure 3.5B shows the temporal evolution of \( r_E/r_B \) ratios in the presence of oxalate. After short reaction times of 1 and 2 h, the \( r_E/r_B \) ratios with oxalate were about at least 15 times higher, and even higher still for dissolved Si and Al after 2 h reaction than those without
added organic ligands (a detailed discussion on anisotropic dissolution is available in 3-S3). The much higher $\frac{r_E}{r_B}$ ratio suggests strong interactions between oxalate and biotite edge surfaces, changing the relative reactivity of biotite edge surfaces and basal surfaces. The ratio decreased to almost same values at 3, 4, 5, and 7 h and, then, further decreased for 8 and 22 h. The decrease of the $\frac{r_E}{r_B}$ ratios resulted from the formation of cracks on basal surfaces (Figure 3.4A3, 4C1–3C3), leading to edge surfaces exposed at the cracked areas on the basal surface, which contributed to the overestimation in basal surface dissolution calculations. During the fitting process, we did not consider the contribution to basal surface dissolution from edge surfaces exposed by cracked regions on the basal surface, which made $r_B$ overestimated and, the ratio $\frac{r_E}{r_B}$ underestimated. However, it is difficult to completely characterize the amount of exposed cracked surface, so there may be some extent of underestimation for the $\frac{r_E}{r_B}$ ratios in the fitting process. With 10 mM acetate (Figure 3.5C), interestingly, there were no significant differences in the $\frac{r_E}{r_B}$ ratios from the case without organic ligands. Hence, oxalate preferentially affects dissolution from biotite edges, but acetate does not. A detailed discussion on the dissolution stoichiometry of the framework ions is available in the section 3-S4 in the supporting Information.
3.3.4 Precipitation of Secondary Minerals on Basal surfaces and Edge Surfaces

Secondary precipitates were observed on both biotite basal surfaces and edge surfaces. Fibrous precipitates appeared on reacted biotite basal surfaces (Figure 3.4). Acetate and oxalate play a role in promoting the formation of fibrous precipitates on basal surfaces, because more fibrous precipitates were observed in the presence of these ligands. To identify the secondary mineral phase on basal surfaces, we conducted HR-TEM measurements (Figure 3-S6). For precipitates detached from biotite reacted with organic ligands, the d-spacing measured from the electron diffraction pattern analyses matched well with those of illite. The observation of fibrous illite was also consistent with what Hu et al. observed for samples reacted under same conditions (95 °C and 102 atm CO₂) as our control experiments.65 With acetate, we observed fibrous illite and platy precipitates from TEM measurement (Figure 3-S6B), although we did not discern platy precipitates in AFM observations. Based on the measured d-spacing, these platy precipitates were also confirmed to be illite. The formation of platy precipitates might be due to slow kinetics in the presence of acetate.

To study secondary precipitation on edge surfaces, we also conducted experiments using thick biotite specimens. Abundant microscale platy and round precipitates were observed on biotite edge surfaces after reaction with 10 mM oxalate. EDX analysis showed these precipitates were rich in Fe (about 20 at. wt %, Figure 3-S7A).
Diffraction patterns (Figure 3-S8) match goethite, magnetite, and maghemite, with quite similar d-spacings. Because oxalate preferentially enhances biotite dissolution from edge surfaces, there would be high ion concentrations around edge surfaces, leading to locally saturated solutions and enabling precipitation. Therefore, oxalate might contribute to secondary precipitation on edge surfaces, especially Fe-enriched minerals. With acetate, reprecipitation of minerals with similar elemental compositions of biotite was observed at biotite edge surfaces (Figure 3-S7B).

3.4 Discussion

3.4.1 Interactions between Acetate and Biotite: pH-induced Mechanisms

To explain acetate’s effects on biotite dissolution, the following mechanisms can be considered. First, acetate might form aqueous complexes with aqueous Al species, and these species will increase the apparent solubility of Al-containing minerals. However, acetate slightly inhibited the dissolution of biotite in our study. Hence, the aqueous complexation between acetate and Al$^{3+}$ may not be the main mechanism for the effects of acetate.

Table 3.1 Final pH of the systems after 96 h reaction, calculated by GWB.

<table>
<thead>
<tr>
<th>Reaction systems</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>No organic ligands, control</td>
<td>4.22</td>
</tr>
<tr>
<td>10 mM acetate</td>
<td>4.32</td>
</tr>
<tr>
<td>10 mM oxalate</td>
<td>4.54</td>
</tr>
<tr>
<td>50 mM acetate</td>
<td>4.19</td>
</tr>
</tbody>
</table>

Second, acetate could possibly affect the solution pH thus impact proton-mediated
biotite dissolution. When pressurized CO$_2$ was injected into the system, the pH dropped to about 3.16 at 95 °C and 102 atm CO$_2$. The addition of acetate could lessen the pH drop, and the higher pH would then decrease the proton-mediated dissolution.$^{137}$ At the same time, secondary precipitation could also be enhanced at higher pH. Decreased aqueous metal concentrations and increased secondary mineral precipitation on biotite surfaces were observed with 10 mM acetate. In the aqueous chemistry, what we observed is the net effect of dissolution and precipitation. Hence, the small difference in pH (Table 3.1, 3-S7) can still be a mechanism that leads to the inhibition effect of acetate on net biotite dissolution. However, with a higher concentration of 50 mM acetate, even though the final pH was lower (pH = 4.19; Table 3.1) the released ion concentrations were lower than with 10 mM acetate experiments (Figure 3.3). Also, compared with experiments using 10 mM acetate, the dissolution of the tetrahedral cations Al and Si decreased more than for the octahedral cations Fe and Mg (Figure 3.3). If the pH buffer effect were the only mechanism, a similar extent of decrease should occur for all the ions. Therefore, considering both aspects in low and high concentrations of acetate, the pH buffer effect can only have a minor contribution in affecting the process. There should be another responsible mechanism impacting biotite dissolution.

Third, the interactions between acetate/acetic acid and surface reactive sites may influence biotite dissolution. Previous studies have shown that acetate can interact with ≡AlOH sites on mineral surfaces,$^{143}$ and also with surface ≡SiOH sites.$^{144}$ The element-specific inhibition effect of acetate shown in Figure 3.3 suggests interactions between acetate/acetic acid and biotite surface Al and Si sites. The pH of our study was lower than the pK$_a$ of acetic acid (pK$_a$ = 4.92, 95 °C), thus acetate was protonated in the reactor and
mainly existed as neutral molecules (~61%, Figure 3-S9). The acetic acid may have adsorbed onto surface $\equiv$AlOH and $\equiv$SiOH sites. At a higher concentration of acetate, more acetic acid molecules would be available to cover more surface $\equiv$AlOH and $\equiv$SiOH sites. The adsorbed layer of organic molecules would have the charged carboxylic groups pointed toward the mineral surface and leave a hydrophobic outer surface. This hydrophobic surface could inhibit the protonation of biotite surface sites, thus reducing the release of Al and Si cations into solution, resulting in element-specific inhibition effects.

As for the secondary precipitation, the higher pH in 10 mM acetate system led to the promoted formation of fibrous illite. Owing to the inhibited dissolution, the dissolution channels formed were shallower with acetate than in control experiments.

### 3.4.2 Interactions between Oxalate and Biotite: Surface Complexation

With 10 mM oxalate, although the pH after 96 h reaction was the highest (pH = 4.54; Table 3.1), the dissolution of biotite was significantly enhanced. The elevated pH may inhibit the dissolution of biotite; however, it is hard to separate the minor inhibition by higher pH from the significant promotion effects on dissolution. Thus, other mechanisms should be considered in oxalate systems. According to the previous studies, in ligand-promoted dissolution, the inner-sphere adsorption of organic ligands on metal oxides and aluminosilicates polarizes and weakens the bond between the surface cations and mineral lattice. Organic ligands whose functional groups contain two or more oxygen donors, and which can form bi- or multidentate mononuclear surface chelates, are especially efficient in promoting dissolution of minerals. Bidentate mononuclear
inner-sphere surface complexes were reported for adsorption of oxalate on goethite, boehmite, and corundum surfaces at acidic pH conditions\textsuperscript{151-152} and were considered intermediate species in the oxalate-promoted mineral dissolution mechanism. Under our experimental conditions, oxalate was the dominant species (~80\%, \textbf{Figure 3-S9}) after 96 h reaction in our study. Thus, we hypothesized that oxalate could form bidentate mononuclear complexes with biotite surface sites. To test the surface complexation, we conducted ATR-FTIR experiments and found that bidentate mononuclear surface complexes between oxalate and Fe and Al sites were indeed formed on the biotite surface (\textbf{Figure 3.6} and \textbf{Table 3.2}, section 3-S8). Therefore, the bidentate mononuclear complexation between oxalate and biotite surface sites can explain the promotion effect on biotite dissolution by oxalate.

\textbf{Figure 3.6} ATR-FTIR spectrum observed for biotite contacted with 1 M NaCl + 10 mM Na$_2$C$_2$O$_4$. The Spectrum of biotite contacted with 1 M NaCl alone was subtracted as the background of the raw spectrum.

\textbf{Table 3.2} Peak frequencies observed in \textbf{Figure 3.6} and from references.\textsuperscript{151-152}
Additionally, the relative reactivities (\(r_E/ r_B\) ratios) shown in Figure 3.5B strongly support the hypothesis that enhancement by oxalate is preferred on biotite edge surfaces by complexing with more reactive sites. Releasing of the complexation between oxalate and edge sites on biotite basal surfaces can possibly influence the internal forces and help relax the vicinity of the chelating spots, creating cracks. The disproportional influence of oxalate on \(r_E\) and \(r_B\) also suggests that aqueous complexations between oxalate and cations are not dominant. If the aqueous complexation effect of oxalate dominated, then \(r_E/ r_B\) ratios similar to those in the control experiments would be expected, because oxalate would not preferentially attack edge surfaces. Therefore, we suggest here three possible steps active in biotite dissolution with oxalate: (1) Oxalate detects edge surface sites of defects on exposed biotite basal surfaces by forming surface chelates, initiating dissolution. (2) Cracks are formed (Figure 3.4C1) through ion-exchange, CO₂ intercalation, and complexation reactions, exposing more edge surface sites on the basal surface to be attacked by oxalate, leading to further dissolution (Figure 3.4C3), and large dissolution channels appear (Figure 3.4C2). (3) Cracked biotite layers peel away from surfaces, exposing new flat basal surfaces (Figure 3.4C4), which then are covered by precipitates (Figure 3.4C5 and

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<th>Peak frequencies observed in experiment (cm⁻¹)</th>
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Peak frequencies observed in experiment (cm⁻¹)Peak frequencies for oxalate-goethite from reference (cm⁻¹)Peak frequencies for oxalate-boehmite from reference (cm⁻¹)
3.4.6. The key mechanism behind the enhancement effect of oxalate is attacking edge surface sites selectively by complexing with edge surfaces.

Due to the enhanced dissolution, the evolution of surface morphological changes of biotite was promoted by oxalate under GCS related conditions. In our experiments at 95 °C and 102 atm CO₂, the formation of cracks and dissolution channels was common. However, previously, Haward et al. studied the dissolution of the basal biotite surface in the presence of 100 mM oxalic acid at temperatures close to ambient conditions. They observed initially slow formation of etch pits in the biotite surface, followed by relatively fast expansion of the etch pits over the surface. In our study, dissolution channels were observed instead, suggesting enhanced dissolution kinetics at high temperature and pressure. Moreover, it was pointed out that CO₂ molecules could penetrate the clay interlayer (i.e., intercalation) and cause swelling and the formation of surface cracks. High temperature, CO₂ pressure, and the presence of oxalate together promote the biotite surface morphological changes, which differ from those in control experiments in our study and the Haward et al. study.

3.4.3 Distinctive Reactivities at Biotite Edge and Basal Surfaces

The preferred edge surface dissolution in the control experiments (Figure 3.5) is consistent with previous studies that edge surfaces are more reactive than basal surfaces for phyllosilicates. The edge surfaces of phyllosilicates are formed with high energy broken bonds and terminated by valence unsaturated oxygen atoms, while oxygen atoms on siloxane-terminated basal surfaces are valence saturated. Therefore, the edge surfaces sites are more reactive and easily attacked by protons. Through the ligand exchange mechanism, oxalate exchanges with H₂O or HO⁻, forming surface complexes.
with biotite surface sites. The subsequent release of the complexes promotes biotite edge surface dissolution. The ligand-promoted dissolution by oxalate hence increased the relative reactivities at biotite edge and basal surfaces.

### 3.5 Environmental Implications

In this study, we provided new information on the effects of acetate and oxalate on biotite dissolution under GCS relevant conditions. Oxalate induced 5–10 time higher release of framework cations than control experiments. The enhanced biotite dissolution caused biotite layers to peel off into the brine solutions, where the layers moved further. Remobilization of biotite particles within the pore space was thought to induce changes in permeability of caprocks. Fibrous illites and iron oxides were observed as secondary minerals in our investigation. The wettabilities of different minerals differ because of mineral-specific surface charge, crystal shape/surface charge anisotropy, and the iron content of the surface layer of minerals. By nature, iron oxides are often considered hydrophilic. However, surface coating of iron oxides leading to oil-wet grain surfaces of sandstone in oil fields was reported. The altered surface morphology (dissolution, precipitates, and roughness) and mineral phases will play roles in the permeability and wettability of rocks, which are important parameters determining the capillary pressure and leakage problem of caprocks.

The new findings of distinctive reactivities of biotite edge surfaces in the presence of organic ligands stresses the importance of considering the structural anisotropy of minerals and organic compounds during GCS operations. At GCS sites, according to previous studies, faults and cracks were reported in low-permeability caprocks where mica
existed, which can potentially expose more edge surfaces and create pathways for brine to contact and react with the minerals in the field sites. Preferential dissolution and secondary precipitation on edge surfaces can alter porosity, permeability, and wettability properties of minerals through the preferential attacked surfaces, impacting the transport and storage of CO$_2$. The presence of oxalate even promoted the reactivities of edge surfaces, strengthening the anisotropic dissolution. Such information has significant implications on understanding and predicting the caprock integrity at GCS sites.

Organic compounds are abundant in deep saline aquifers and also in depleted oil/gas reservoirs. Hence, the results reported in this study can benefit safer and more efficient GCS and CO$_2$-EOR operations and other energy-related subsurface engineering operations.

**Acknowledgments**

We are grateful for support received from NSF CAREER AWARD (EAR-1057117) and Washington University’s Consortium for Clean Coal Utilization. We would like to acknowledge Washington University’s Center for Materials Innovation (CMI) for use of HR-TEM and the Nano Research Facility (NRF) for use of SEM-EDX. We would also like to thank Doyoon Kim for HR-TEM measurements.
Supporting Information for Chapter 3

3-S1. Residual organic ligands in reaction system

The aqueous concentrations of acetate and oxalate decreased during the reaction. Shao et al. suggested that the decrease of acetate concentration is due to the extraction of acetic acid by scCO$_2$.\textsuperscript{137} This could also explain our experimental result, because at the pH condition of our experiment, acetate exists as acetic acid, as discussed in the main paper. As to the decrease of oxalate, there were three possible processes responsible for this phenomenon. First, oxalate might have decomposed as the reaction went on. Based on the decomposition rate constant of oxalate at 160 °C at pH 3.7 ($4.31 \times 10^{-6}$ per second) and the activation energy of about 27.6 kcal/mol provided by Crossey,$^162$ we estimated the concentration of decomposed oxalate under the experimental conditions in our study. However, the results showed that at 95 °C, after 96 h of reaction, less than 0.5% oxalate has degraded. Second, oxalic acid might have been transported into the scCO$_2$ phase. As previously mentioned, supercritical CO$_2$ can be used to extract oxalic acid in aqueous solutions.$^163$ Third, oxalate might have adsorbed onto biotite surface and formed surface complexes.

![Figure 3-S1](image)

**Figure 3-S1** Residual concentrations of organic ligands in the brine vs. elapsed reaction time.
3-S2. Additional AFM analyses

(A)

(B)

Figure 3-S2 (A) Height image collected in AFM contact mode; (B) Height profile of crack on biotite surfaces after reaction with 10 mM oxalate for 8 h. The size of the AFM image is 50 μm × 50 μm. The height profile is cut along the white dotted line.

Figure 3-S3 Average depth of dissolution channels on reacted biotite basal surfaces.

Statistical analyses of the height of the precipitates and depth of cracks were made from the AFM images. For every sample, four AFM contact mode images were collected. The depth of the dissolution channels and the height of the fibrous precipitates were taken from the average of 80 spots from the four representative AFM images. Figure 3-S3 shows the results of the statistical analyses for the crack depth. For the control samples, cracks started to form after 22 h reaction. In the presence of 10 mM acetate, cracks were lower than in control samples. Peeling of surface layers was observed for 96 h control samples,
therefore the crack depth was similar to that of the acetate samples. In the presence of 10 mM oxalate, cracks were observed within 3 h reaction. After 22 h, cracked biotite layers detached from surface, making the remaining crack depth lower than 8 h with oxalate. After 70 and 96 h reaction with oxalate, the newly exposed basal surface was covered by precipitates and no cracks were observed.

![Image 1](image1.png)  ![Image 2](image2.png)  ![Image 3](image3.png)

Figure 3-S4 A1-3 and B1-3 are height, deflection, and friction AFM images collected in contact mode for images C5 and C6 shown in Figure 3.4 in the main paper, respectively. The size of the images is 50 µm x 50 µm. The height scale is 100 nm for A1 and 200 nm for A2. The scale of the deflection and friction images is 700 mV. Because the surface was too rough due to the precipitates (~100 nm high), AFM could not resolve well. But if we consider all the height, deflection, and friction images, it is clear that there are secondary precipitates formed on biotite basal surfaces after 70 and 96 h reaction with 10 mM oxalate.

3-S3. Anisotropic dissolution of biotite

The significant increase of dissolved Si and Al in the 10 mM oxalate system after 2 h of reaction might be due to the preferential attack by oxalate on edge surfaces. The formation of surface complex between oxalate and Al will lead to the release of Al, and subsequent release of tetrahedral Si. In addition, the dissolution of debris or small biotite particles, which could not be fully removed and remained among the biotite flakes, can also lead to the fast initial dissolution. Smaller biotite particles have higher surface area and exposed higher percentage of edge surfaces to be attacked by oxalate than bulk biotite.
3-S4. Biotite dissolution stoichiometry

The interlayer K was obviously preferentially released over framework cations in different reactor compositions, considering much higher K concentrations. The concentrations of released framework cations presented in the following figures are normalized by the chemical formula of biotite). The dissolution of biotite was incongruent for all three systems (control, acetate, and oxalate) in our experimental systems. The release of Al was preferred over other framework cations (Si, Fe, and Mg) as shown in the figures.

Oxalate preferentially attacked edge surfaces and a difference of dissolution stoichiometry would be expected. However, the biotite flakes used in this study have a length of about 2.0 cm, width of 0.8 cm, and thickness of 80 µm. If we consider that the exposed edge surface area (~4.5 mm$^2$) was much lower than the basal surface area (~320 mm$^2$), the effect of oxalate on specific elemental dissolution from edge planes may not be discernable in the overall dissolution stoichiometry analyses. In addition, please note that the dissolved elemental concentrations showed net concentrations (total dissolved concentrations minus concentrations removed by secondary mineral formations). The release of Fe in the control system at longer reaction time (96 h) was faster than Al, Si, and Mg, but if we consider the experimental error range, it still follows the trend.

Here, please also note that in our group’s previous publication, the dissolution of biotite framework cations was congruent at 95 °C and 102 atm CO$_2$ with 1 M NaCl.\textsuperscript{78} Between this work and the previous work, all other conditions were identical, but the biotite specimens were different as shown in experimentally determined chemical formula. Thus, the dissolution stoichiometry could be slightly different due to the different biotite samples used and the locality where the biotite samples were originated.
Figure 3-S5 Normalized ion concentrations by biotite chemical formula after reaction in (A) control, (B) 10 mM acetate, (C) 10 mM oxalate systems under 95 °C and 102 atm CO₂.
3-S5. HR-TEM identification of secondary minerals on basal surfaces

(A) Control, no organic ligands

(B) 10 mM acetate
**Figure 3-S6** HR-TEM characterization of secondary mineral phase on biotite basal surfaces after reaction without organic ligands (A), with 10 mM acetate (B), and with 10 mM oxalate (C) under 95 °C and 102 atm CO₂, with an ionic strength of 1.0 M and initial pH of 3.16. The tables of electron diffraction (ED) patterns correspond to the spots indicated by the white boxes in the left images, respectively. For all three cases, fibrous precipitates were observed and identified as illites. In the 10 mM acetate case (B), we also observed platy precipitates (lower image in B), which were also identified as illites.

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3-S6. Identification of secondary minerals on biotite edge surfaces

Scanning electron microscopy with Energy-dispersive X-ray spectroscopy (SEM-EDX)

(A) 10 mM oxalate

(B) 10 mM acetate

Figure 3-S7 SEM observations of the edge planes of thick biotite crystals after reaction at 95 °C and 102 atm CO₂ for 7 days with 10 mM oxalate (A) and with 10 mM acetate (B). EDX measurements were performed at the spots indicated by the red boxes, and the atomic percentages of the elements are shown.
High Resolution-Transmission Electron Microscopy with Electron Diffraction (HR-TEM-ED)

We also conducted HR-TEM experiments to identify the secondary mineral phase after reaction with 10 mM oxalate. The precipitates were detached by sonication from edge surfaces of thick biotite crystals prepared by 7 days reaction at 95 °C and 102 atm CO₂ for 7 days. The TEM sample preparation process is similar to that described in the experimental section in the main paper. The TEM results are showed in Figure 3-S8.

Figure 3-S8 HR-TEM measurements of secondary mineral phases on biotite edge surfaces after 7 days reaction with 10 mM oxalate at 95 °C and 102 atm CO₂, with an ionic strength of 1.0 M and initial pH of 3.16. (A) and (B) are images of two representative kinds of precipitates, and the tables are the corresponding electron diffraction (ED) analyses of spots indicated by white boxes in the upper images. Biotite was ruled out from the measured d-spacings, and A matches goethite. Because the structures of magnetite and maghemite are similar, d-spacings measured for B were shared by magnetite and maghemite. B could be either magnetite or maghemite, or both of them.
3-S7. GWB thermodynamic calculations

(A)

Figure 3-S9 Speciation diagram of acetate and oxalate. The speciation of (A) acetate and (B) oxalate as a function of pH was also calculated by GWB. The final pH of 10 mM acetate and 10 mM oxalate is indicated by the dotted line. After 96 h reaction in the 10 mM sodium acetate system, approximately 61% is acetic acid. And in the 10 mM sodium oxalate system after 96 h reaction oxalate is the dominant species, with a fraction of 80%.
3-S8. Fourier transform infrared (FTIR) spectroscopy analyses of oxalate adsorption on biotite surfaces

The ATR-FTIR spectrum of biotite contacted with solution (b) is shown in Figure 3.6, with the spectrum of biotite contacting with solution (a) subtracted as background. The observed peak frequencies are listed in Table 3.2. From previous studies, peak frequencies of 1713, 1689, 1389, and 1246 cm\(^{-1}\) were observed for bidentate mononuclear surface complexes between oxalate and Fe sites on goethite (\(\alpha\)-FeOOH) surfaces.\(^{151}\) Peak frequencies of 1720, 1700, 1418, and 1286 cm\(^{-1}\) were observed for bidentate mononuclear surface complexes between oxalate and Al sites on boehmite (\(\gamma\)-AlOOH) surfaces.\(^{152}\) Table 3-S2 shows that the peak frequencies in our study were compatible with those reported peak frequencies. For example, peak frequencies of 1725, 1685, 1382, and 1251 cm\(^{-1}\) were close to peak frequencies reported in the literature for oxalate bidentate mononuclear surface complexes with Fe sites on goethite surfaces. Peak frequencies of 1725, 1685, 1409, and 1270 cm\(^{-1}\) were close to those reported for oxalate bidentate mononuclear surface complexes with Al sites on boehmite. Therefore, they can be assigned to bidentate mononuclear surface complexes between oxalate and Fe and Al sites on biotite surfaces. However, the peak frequencies for oxalate-Fe and oxalate-Al are quite close. The chemical formula of the biotite used in this study was K\(_{0.91}\)Na\(_{0.08}\)Ca\(_{0.05}\)(Mg\(_{0.57}\)Mn\(_{0.02}\)Fe\(_{0.34}\)Ti\(_{0.04}\))\(_3\)(Al\(_{1.00}\)Si\(_{3.00}\))O\(_{10}\)(F\(_{0.51}\)(OH)\(_{0.49}\))\(_2\), with an Fe/Al ratio of 1.02. Hence, we concluded that a combination of surface complexes between oxalate and Fe and Al sites on biotite surfaces existed, and significantly enhanced biotite dissolution.
Chapter 4. Effects of Phosphate on Biotite Dissolution and Secondary Precipitation under Conditions Relevant to Engineered Subsurface Systems

The results of this chapter have been published in *Physical Chemistry Chemical Physics*, 2017, 19, 29895-29904.

**Abstract**

Inorganic phosphate, an important oxyanion in brine, can strongly complex with mineral surfaces and form secondary precipitates. Phosphate naturally exists at low concentrations in subsurface brines, and its concentration can be increased significantly during energy-related engineered subsurface processes. Thus, in this chapter, we further investigate the impact of phosphate anions on brine–mica interactions under subsurface conditions. Biotite dissolution experiments were conducted without and with phosphate (0.1, 1, and 10 mM) at 95 °C and 102 atm CO₂. Compared to the control, 0.1 mM, and 1 mM phosphate systems, biotite dissolution was four times higher with 10 mM phosphate. Despite the dissolution differences, in all the phosphate systems, phosphate interacted with Al and Fe sites in biotite, forming surface complexation and precipitating as Fe- or Al-bearing minerals on surfaces and in solutions. Consequently, aqueous Fe and Al concentrations became lower with phosphate than in the control experiments. In addition, the biotite basal surfaces became more hydrophilic after reaction with phosphate, even at
0.1 mM, mainly from phosphate adsorption. This study offers new information on how phosphate-containing brine interacts with caprocks and on the consequent wettability changes, results that can benefit current and future energy-related subsurface engineering processes.

4.1 Introduction

Energy-related subsurface operations, such as geologic CO₂ sequestration (GCS) and CO₂-enhanced oil/gas recovery, are promising strategies to mitigate global warming and meet energy demands.¹ ¹⁶⁶ Both strategies include CO₂ injection at subsurface sites,¹,¹¹² where the temperature and pressure can range between 31–110 °C and 73.8–600 atm, respectively.⁵⁻⁷ After injection, CO₂ stays in its supercritical phase (scCO₂) or dissolves in brine, forming H₂CO₃ and HCO₃⁻ aqueous species and releasing H⁺. A caprock layer at the site serves as a seal, hindering the upward movement of injected CO₂. The efficacy of the layer is largely governed by capillary pressure.¹⁰⁶ As denoted in the Young-Laplace equation,

\[ P_c = P_{CO2} - P_w = \frac{2\gamma_{we} \cos \theta}{R} \]

the capillary pressure \( P_c \), i.e., the pressure difference between CO₂ pressure \( P_{CO2} \) and water pressure \( P_w \), is dependent on the scCO₂–brine interfacial tension \( \gamma_{we} \), pore radius \( R \), and wettability \( \theta \). During GCS, to store CO₂ in reservoir rock pore spaces initially occupied by brine, the CO₂ pressure should exceed the capillary pressure and displace the brine; later, brine can again substantially replace CO₂, leaving some trapped in the pore spaces by capillary forces.³⁵⁻³⁷ On the other hand, the sealing of the caprock layer fails if the CO₂ pressure there exceeds the capillary pressure, in which case CO₂ will leak.
Owing to the high temperature, pressure, and salinity in subsurface sites, and to the low initial pH induced by injected CO₂, dissolution of reservoir or caprock minerals and secondary mineral precipitation can occur. Mica is a group of abundant minerals in caprocks at subsurface sites, with a mass fraction of about 30% in the Sleipner shales in Norway and 10–33% in the Venture gas field in Canada. Recent studies report that mica can react with scCO₂-saturated brine, subsequently affecting the geophysical properties of caprocks and creating CO₂ leakage pathways. Such interactions between brine and minerals may alter the porosity, permeability, or wettability of the rocks related to the capillary pressure, thus influencing the sealing of the caprock layer. Because the integrity of the caprock layer is essential to the long-term subsurface storage of CO₂, a better understanding of the effects of brine chemistry on chemical reactions of mica under relevant conditions is needed to ensure safe and efficient subsurface operations.

At subsurface sites, both inorganic and organic ligands are abundant in brine. The effects of organic ligands, such as acetate and oxalate, on mineral dissolution have been investigated under subsurface conditions. For example, acetate slightly inhibited the dissolution of feldspar and biotite, however, oxalate significantly enhanced biotite dissolution. Among inorganic ligands, phosphate is reported in subsurface brine with concentrations between 0.5–20 μM. It is well known that phosphate has a strong surface complexation capacity under ambient conditions and can adsorb onto mineral surfaces, such as aluminum or iron (hydr)oxides. In addition, phosphate can precipitate with aluminum or iron ions in acidic solutions or oils. Both the adsorption and precipitation triggered by phosphate may disturb the water–mineral equilibrium and cause the minerals
to dissolve and undergo phase transformation. Further, phosphate can interact with mica minerals, which have more complicated structures than metal (hydr)oxides.

The phosphate surface complexes mentioned above have several configurations, such as monodentate mononuclear, bidentate mononuclear, or bidentate binuclear, depending on experimental conditions such as ionic strength and pH.\textsuperscript{50-51, 170-172} The configurations of surface complexes have different effects on mineral dissolution.\textsuperscript{98, 147-148, 173} For example, monodentate and bidentate mononuclear complexations are expected to promote mineral dissolution by polarizing and weakening the bonds between the surface cations and mineral lattice, whereas bidentate binuclear complexation can inhibit mineral dissolution as a result of the large activation energy required to release the two metal centers and the lack of surface protonation at uncharged binuclear sites.\textsuperscript{147-148, 173-174} The influenced dissolution will further impact the saturation conditions of potential minerals in the system, thus affecting secondary precipitation. Despite the importance of surface complexation, the influences of adsorbed phosphate on mica minerals on their consequent dissolution and secondary mineral precipitation under subsurface conditions have not been evaluated.

In addition to naturally occurring phosphate, phosphonate-based scale inhibitors, such as diethylenetriaminepenta(methylene phosphonic acid) (DTPMP), are widely used in subsurface engineering processes, such as conventional and unconventional oil/gas production or geothermal operations.\textsuperscript{175-176} The average concentration of phosphonate scale inhibitor is about 0.023wt\% (0.5 mM). They contain two or more phosphonate functional groups with a strong complexation capability,\textsuperscript{177} similar to phosphate, which can also affect mineral dissolution and secondary precipitation.\textsuperscript{176} Furthermore, microorganisms or
oxidizing biocides used to control microbiological growth in hydraulic fracturing can degrade phosphonates into orthophosphate, increasing the concentration of orthophosphate to around 1–2 mM. Hence, an investigation of the effects of phosphate on brine–mica interactions can be a good starting point to better understand the effects of naturally occurring inorganic ligands and provide new information about the potential effects of phosphonate-based scale inhibitors in energy-related subsurface operations.

Moreover, chemical reactions between phosphate and mica, including adsorption, dissolution, and secondary precipitation, can cause wettability changes in mica by changing the physico-chemical properties of surfaces. As we described earlier, the wettability of mineral surfaces, usually expressed by contact angles (θ), can largely determine the mobility, migration, and distribution of reactive fluids, and thus it is an important parameter for engineered subsurface operations. The hysteresis in the contact angle can also be a good indicator of the residual trapping capacity of CO₂, both during injection and post-injection. In our previous study, we found that higher salinity can enhance biotite dissolution, inducing a rougher surface, more surface charge, and a higher density of surface hydroxyl groups. Consequently, the biotite became more hydrophilic under subsurface conditions. Likewise, the interactions between phosphate and mica minerals may change the mineral surface morphology and mineralogy, leading to wettability alteration. Nevertheless, how phosphate affects mica wettability is still unknown.

Therefore, the objective of the present study is to provide mechanistic understanding of the physicochemical effects of phosphate on biotite dissolution and secondary precipitation, and to link chemical reactions with the wettability change of biotite under high temperature and high pressure (95 °C and 102 atm CO₂) conditions.
Biotite was chosen as a model caprock mineral, as in previous studies. For the first time, this study identifies the significant roles of phosphate in brine–mineral interactions and the subsequent distinctively enhanced biotite wettability. Ultimately, the explicit information of physical chemistry of phosphate in a wide range of concentrations obtained from this single-mineral system can be useful for better interpreting complex reaction systems, and can also benefit other current and future engineered subsurface processes in addition to GCS.

4.2 Experimental Section

4.2.1 Minerals and Chemicals

The composition of biotite purchased from Ward’s Natural Science was analyzed with X-ray fluorescence (XRF) and found to be K_{0.91}Na_{0.08}Ca_{0.08}Mg_{1.72}Mn_{0.06}Fe_{1.12}Ti_{0.12}Al_{1.00}Si_{2.98}O_{10}(F_{0.51}(OH)_{0.49})_2 (Table 2.1). Biotite flakes with a thickness of 80 ± 10 µm (measured by a Vernier caliper) were cleaved along the {001} basal planes with a razor blade and cut into 2.0 cm × 0.8 cm rectangles. The biotite flakes were sonicated successively in acetone, ethanol, and isopropanol, each for 5 minutes, to remove organic contaminants, then washed with deionized (DI) water (resistivity > 18.2 MΩ·cm, Barnstead ultrapure water systems). Finally, they were dried with high purity nitrogen gas for high temperature and high pressure experiments.

All chemicals used in this study were ACS grade or higher. At subsurface sites, the brine usually has a salinity between 0.01–2.2 M. Hence, a background salinity of 1 M NaCl was used to simulate subsurface conditions. To examine the effects of phosphate, initial phosphate concentrations of 0 (control), 0.1, 1, and 10 mM were prepared by adding
disodium phosphate to 1 M NaCl solution. The two relatively higher concentrations (1 and 10 mM phosphate) were chosen to facilitate observations by laboratory instruments (e.g., Fourier transform infrared spectroscopy). These concentrations can also be found in localized environments or subsurface sites where phosphonates degrade and consequently release a high amount of phosphate.

4.2.2 High Temperature and High Pressure Reactions

Biotite dissolution experiments were conducted in a 300 mL high temperature and high pressure reactor (Parr Instrument Co., IL, Figure 2.1) used in our previous studies. Generally, at subsurface sites, the temperature and pressure depend on the depth, with the relationships $T (°C) = 15 + 33 d$ and $P (atm) = 1 + 100 d$ ($d$ is depth in kilometers). We used a pressure of 102 atm CO$_2$ to simulate field site pressure at a depth of about 1 km, which is within the depth range of subsurface sites used for engineered operations. However, the experimental temperature was 95 °C, which was higher than the temperature at 1 km depth. By using a relatively high temperature to trigger fast reactions, we made observations available within a reasonable experimental time and could also compare the data with previous studies conducted in a similar temperature range. The pH of the control system was 3.16, assuming equilibrium at 95 °C and 102 atm of CO$_2$, as calculated by Geochemist’s Workbench (GWB, Release 8.0). The relevant thermodynamic calculations can be found in 4-S1 in the Supporting Information for Chapter 4. Thus, the initial pH of the solutions with phosphate was adjusted prior to CO$_2$ injection, which gave the systems the same pH value as the control system without phosphate (pH = 3.16 at 95 °C and 102 atm of CO$_2$). The pH adjustment was conducted using diluted trace metal hydrochloric acid (HCl, BDH) and sodium hydroxide (NaOH, BDH). The addition of HCl
and NaOH did not much affect the ionic strength due to the pre-existing high concentration of NaCl (1 M) used. The experimental conditions mimicked the GCS conditions in the early period of CO₂ injection and at injection zones close to the injection well. Biotite flakes were reacted in the prepared solutions for the desired time intervals (3, 8, 22, 44, 70, and 96 h). After reactions, the solutions were filtered through 0.2 µm polypropylene membranes and acidified in 1% trace metal nitric acid. The aqueous solutions were analyzed with inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 7300 DV) for the dissolved concentrations of biotite components (K, Al, Fe, Si, and Mg), and with ion chromatography (IC) for the residual phosphate concentration in the solutions. The pH values after 22 h and 96 h reactions were calculated by taking the ICP-OES and IC results as the input for GWB calculations. In this calculation, we assumed that the concentration of Cl⁻ did not change much, but the loss of the Na⁺ equals to the release of K⁺ because of cation-exchange reactions between Na⁺ and biotite interlayer K⁺. Then the cation activities, pH values, and saturation ratios of minerals were obtained.

4.2.3 Characterization of Reacted Biotite Samples

The reacted biotite flakes were rinsed with DI water as soon as they were taken from the reactor and dried with high purity nitrogen gas. The rinsed reacted biotite flakes were mounted onto steel pucks and placed on sample stage, and then measured with atomic force microscopy (AFM, Nanoscope V Multimode SPS, Veeco) for surface morphology. AFM measurements were conducted under ambient conditions in contact mode. Areas of 50 µm by 50 µm were scanned at a rate of 0.999 Hz and a deflection set point of 1.975 V, using nonconductive silicon nitride probes (tip radius of 10 nm, DNP-S10, Bruker).
collected AFM images were analyzed with Nanoscope software (v7.20). Root-mean-square surface roughness ($R_q$) is defined as $R_q = \frac{1}{L} \int_{0}^{L} |Z(x)|^2 dx$, where $Z(x)$ is a function that describes the surface profile analyzed in terms of the height ($Z$) and position ($x$) of the sample over the evaluation length $L$. We used this definition as an indicator of surface roughness. The reported roughness was calculated from at least four obtained AFM images for each sample.

To prepare samples for scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX, Nova NanoSEM 230), biotite flakes reacted with 10 mM phosphate for 70 h were collected, carefully rinsed, and dried as before prior to the measurements. The samples were coated with AuPd, and a 10.00 kV electron accelerating voltage was used for the measurements. High resolution-transmission electron microscopy (HR-TEM, JEOL-2100F) was also used to characterize precipitates in solutions and on biotite basal surfaces after 22 h and/or 96 h reactions. For imaging precipitates on biotite basal surfaces, biotite debris with secondary precipitates was detached from sample surface using sonication in ethanol for 5 min and a droplet of the suspension was placed on a Formvar/carbon coated-Cu TEM grid (Electron Microscopy Science, PA). To image precipitates in the solution, the solution after reaction was centrifuged at 5000 rpm for 5 min, and the supernatant containing dissolved ionic species was discarded. DI water was then added to the centrifuge tube, which was centrifuged for another 5 min. This process was repeated five times, until no ionic species were detected in the supernatant solutions. A droplet was then taken from the bottom of the solution (containing only particles formed during the reactions) and placed on a TEM grid. In this way, all detectable ionic species were removed to prevent unexpected precipitation during the drying process, which might
affect TEM characterization. To identify the phase of the secondary precipitates formed during high temperature and high pressure reactions, we obtained the lattice fringes, electron diffraction patterns, and elemental compositions by energy dispersive X-ray spectroscopy during TEM measurements.

Under ambient conditions, using a contact angle analyzer (Surface Electro Optics, Phoenix 300), contact angles (CA) were measured with DI water for biotite samples reacted in the control, 0.1 mM, 1 mM, and 10 mM phosphate systems at 95 °C and 102 atm of CO₂ for 70 h (Figure 4.1 and 4-S2). Additional biotite flakes with dimensions of 2.5 cm × 2.5 cm × 80 µm were prepared and reacted in control and 10 mM phosphate solutions for 70 h. The reacted biotite flakes were then measured for contact angles with a customized apparatus (Figure 2.2) under high temperature and high pressure. The measurement conditions were kept at 48 ± 1 °C and 102 atm of CO₂, to mimic subsurface conditions and to have a low enough temperature to avoid additional reactions during measurements. As confirmed in our recent study using AFM, there was no discernible alteration of biotite basal surfaces under these conditions. Therefore, the CA differences resulted solely from the pretreatment reactions. Both static CA and dynamic CA were measured using a captive drop method by passing scCO₂ through a needle to form a droplet on the mineral surface in an upside-down chamber (the detailed measurement process can be found in 2-S2). During dynamic CA measurements, scCO₂ was slowly added to or withdrawn from the droplet on the sample surface through the needle tip located near the sample surface. This process was recorded by a camera. For each sample, five to eight measurements were performed, and CAs of scCO₂ were directly measured from the images obtained with a high-resolution time-lapse camera (6.2 Megapixel, Nikon D7000). Water CAs were
obtained by subtracting the scCO$_2$ contact angles from 180 degrees, and the average CAs of the water phase were reported. The length of the contact line, i.e., the ternary phase line among biotite, CO$_2$, and brine, was measured at the last moment of the CO$_2$ receding process, just before CO$_2$ detached from the needle (Figure 4.1).

Figure 4.1 (A) Image taken during ambient condition contact angle measurements. (B) Contact angle measurement process under high P/T conditions.

4.2.4 Fourier Transform Infrared (FTIR) Spectroscopy

Analyses of Phosphate Complexation

Attenuated total reflectance (ATR)-FTIR spectra were collected using a Thermo Scientific Nicolet iS10 spectrometer with a horizontal Ge ATR crystal to investigate the types of phosphate-biotite surface complexes. Clean biotite flakes were first ground in a grinder with stainless steel blades in dry condition for half an hour, and then particles in
the size range of 53–106 µm were collected with sieves. The biotite particles were sonicated in ethanol for half an hour to detach tiny particles, and the suspension was allowed to settle for 3 hours. The supernatant was collected, and the size of the particles was measured by dynamic light scattering as around 100 nm. The time periods for sonication and settlement were tried many times to get the final particle size to be around 100 nm. The particles were suspended in ethanol, deposited onto the Ge crystal, and allowed to dry. Solutions were prepared of (a) 1 M NaCl, (b) 1 M NaCl + 1 mM phosphate, and (c) 1 M NaCl + 10 mM phosphate. All three solutions had a pH of 3.16, which is the initial pH under conditions of 95 °C and 102 atm of CO₂. Next, 1 mL of the prepared solution was added to the crystal and allowed to contact the dried biotite particle film. An average of 400 scans at a resolution of 1 cm⁻¹ was used. To obtain phosphate complexation information, the spectrum of biotite contacting solution (a) was used as a background and subtracted from the spectra of biotite contacting solutions (b) and (c). The observed spectra were normalized by the highest absorbance in the region of interest (1200–950 cm⁻¹) and the spectrum of 10 mM phosphate sample was offset to show the features of the two spectra.

4.3 Results and Discussion

4.3.1 Concentration-dependent and Element-specific Effects of Phosphate on Biotite Dissolution

The effects of phosphate on biotite dissolution under conditions relevant to subsurface environments are phosphate concentration-dependent and element-specific, as shown in Figure 4.2. Due to similar extents of ion-exchange reactions, the concentrations of K⁺ in the solutions were almost the same for all reaction systems (0, 0.1, 1, and 10 mM
phosphate) after biotite dissolution within 96 h. The release of K$^+$ is mainly through ion-exchange reactions with H$^+$ or Na$^+$ in the solution. The ionic strength of the reaction solutions was controlled to be about 1.0 M NaCl. In addition, the final pH values (96 h) of the reaction systems simulated by GWB were 3.43, 3.30, and 3.52 for the control, 1 mM phosphate, and 10 mM phosphate systems, respectively (Table 4.1). Therefore, we suggest that the similar concentrations of aqueous K$^+$ observed in the three systems resulted from similar extents of ion-exchange reactions occurring. On the other hand, after reaction with 10 mM phosphate, the concentrations of Si and Mg were about 3–4 times higher than in the control experiments, while the effects of 1 mM phosphate were not discernible. Unlike the Si and Mg cases, after about 20 h, the aqueous concentrations of Al were lower in the 1 mM and 10 mM phosphate systems than in the control system. As for the evolution of aqueous Fe, in the early stage (i.e., reactions time shorter than 44 h), the concentration was higher in the 10 mM phosphate than in the control. In the later stage, reaction times of 44 h and longer, the concentrations of Fe became lower for 1 mM and 10 mM phosphate systems than that in the control. At an even lower phosphate concentration of 0.1 mM, after 44 and 70 h reaction, while the aqueous Si and Mg concentrations were close to those of the control, lower Fe and Al concentrations were still observed, further suggesting the concentration-dependent and element-specific effects of phosphate.
Table 4.1 Calculated pH values and saturation indices with respect to potential secondary mineral phases after 22 and 96 h reaction time.

<table>
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<tr>
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<th>22 h</th>
<th>96 h</th>
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<tr>
<td>pH</td>
<td>Mineral saturation states</td>
<td>pH</td>
</tr>
<tr>
<td></td>
<td>(log Q/K)</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>3.27 Goethite: 5.47; Gibbsite: -0.11; Illite: &lt;-3</td>
<td>3.43 Goethite: 6.41; Gibbsite: 0.73; Illite: -1.9</td>
</tr>
<tr>
<td>1 mM phosphate</td>
<td>3.24 Strengite: 3.07; Berlinite: 0.67; Gibbsite: -0.74; Illite: &lt;-3</td>
<td>3.30 Strengite: 3.4; Berlinite: 0.9; Gibbsite: -0.5; Illite: &lt;-3</td>
</tr>
<tr>
<td>10 mM phosphate</td>
<td>3.31 Strengite: 4.63; Berlinite: 2.3; Gibbsite: -0.04; Illite: &lt;-3</td>
<td>3.52 Strengite: 5.0; Berlinite: 2.4; Gibbsite: 2; Illite: -0.1</td>
</tr>
<tr>
<td>20 µM phosphate</td>
<td>3.24 Strengite: 1.38; Gibbsite: -0.72; Diaspore: 0.06; Illite &lt; -3</td>
<td>3.31 Strengite: 1.8; Gibbsite: -0.42; Diaspore: 0.36; Illite: &lt; -3</td>
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</table>

Figure 4.2 Aqueous concentrations of K, Al, Si, Fe, and Mg from biotite dissolution at T = 95 °C and P_{CO2} = 102 atm, with a salinity of 1.0 M NaCl and initial pH of 3.16, in 0, 0.1, 1, and 10 mM phosphate solutions. Error bars are the standard deviation of triplicate samples. The dominant reactions over time in the presence of phosphate are indicated at the bottom of the figure.
To mechanistically explain the effects of phosphate on the evolution of framework cations, three aspects were considered: First, aqueous complexation between phosphate and cations can increase apparent solubility, enhancing biotite dissolution. However, the UV-Vis absorbance of phosphate aqueous complexation was weak (Figure 4-S1). Therefore, aqueous complexation was not the main mechanism of the phosphate effects. Second, surface complexation can play a role. Phosphate can interact with surface Fe and Al sites through bidentate mononuclear or monodentate mononuclear complexation, promoting their release into solutions, and subsequently promoting the dissolution of Si and Mg, with stronger surface complexation in the presence a higher phosphate concentration. However, the aqueous Fe and Al concentrations were low at later reaction stages with phosphate. Hence, in addition to surface complexation, secondary precipitation was considered because the precipitation of Fe- or Al-bearing secondary phases can lower the aqueous concentrations of Fe and Al. Note that the ion concentrations shown in Figure 4.2 measured by ICP-OES are the net concentrations from dissolution and secondary precipitation. We assumed that 0.1 mM and 1 mM phosphate did not greatly promote biotite dissolution, and we further assumed that 10 mM phosphate promoted the release of Al and Fe, as it did for Si and Mg. After longer reaction times (44 h for Fe and 22 h for Al), secondary precipitation became dominant. Significant secondary precipitation of Fe- or Al-bearing minerals in the solution or on biotite surfaces could explain their observed lower aqueous concentrations. Secondary mineral precipitation, removing Fe and Al cations from the solution, can further promote forward mineral dissolution. Therefore, we postulated that surface complexation and secondary precipitation could be mechanisms responsible for the concentration-dependent and element-specific effects of phosphate.
Thermodynamic calculations show that after 22 h and 96 h reactions, the 1 mM and 10 mM phosphate systems are saturated with Fe- and Al-bearing minerals, and that the saturation indices increase as reaction continues (Table 4.1), consistent with our hypotheses. To support the mechanisms of the phosphate effects on aqueous cation evolutions, we conducted further investigations on surface properties using AFM.

4.3.2 Effects of Phosphate on the Surface Morphological Changes of Biotite

The AFM images in Figure 4.3 show that biotite basal surface morphological changes over time were significantly affected by 10 mM phosphate, while samples reacted with 1 mM phosphate had morphology similar to the control samples. Consistent with our recent reports, we observed the formation of cracks on biotite basal surfaces, caused by ion-exchange reactions and CO₂ intercalation, after 22 h reaction in the control experiment.65, 79 With 1 mM phosphate, cracks formed as in the control samples, with similar crack depths (Figure 4-S2). However, with 10 mM phosphate, cracks were observed within 8 h reaction (Figure 4.3C), indicating that 10 mM phosphate promoted biotite dissolution. Moreover, as AFM images show (Figure 4.3C), biotite basal surfaces were significantly covered by secondary precipitates after reaction with 10 mM phosphate, increasing the surface roughness. For example, after 22 h reaction, the root-mean-square surface roughness values, given by AFM measurements of scan areas of 50 µm × 50 µm, were 4.7 ± 1.4 nm, 7.0 ± 1.8 nm, and 26.8 ± 3.2 nm for the control, 1 mM phosphate, and 10 mM phosphate samples, respectively. Due to the high surface roughness resulting from coverage by a large quantity of secondary precipitates with 10 mM phosphate, AFM could
not resolve the surface features clearly. Thus, a complementary tool, SEM, was used to clearly show the biotite basal surface after reaction with 10 mM phosphate for 70 h. As seen in the inset in Figure 4.3C_70 h as well as Figure 4.5C, the biotite surface was covered by a thin film of amorphous phases underneath the round particles. The diameters of the round particles were up to 200 nm, and EDX analysis showed that the round particles were more abundant in Fe and Al than the raw biotite material (Figure 4-S3).

By relating microscopic observations to the ICP-OES results, we found that 10 mM phosphate promoted biotite dissolution and consequent secondary precipitation. The surface precipitation of Fe- and Al-bearing phases became more dominant as the reaction time increased and it contributed to lower aqueous concentrations of Fe and Al with 10 mM phosphate than in the control system. Precipitates formed in the 10 mM phosphate solution could also reduce the aqueous Fe and Al concentrations. For the 1 mM phosphate samples, while we could not observe significant precipitation by AFM, secondary precipitation could still have occurred either on biotite surfaces or in the solution, because the results from ICP-OES revealed lower aqueous Fe and Al concentrations. To further investigate phosphate complexation and the phases of secondary precipitates, and to provide additional information to illuminate the mechanisms of phosphate effects, experiments with ATR-FTIR and HR-TEM were conducted.
Figure 4.3 AFM observations of biotite basal planes after reaction at $T = 95 \, ^\circ C$ and $P_{CO_2} = 102$ atm, with a salinity of 1.0 M NaCl and initial pH of 3.16, without phosphate (A), with 1 mM phosphate (B), and with 10 mM phosphate (C). AFM images (50 $\mu$m $\times$ 50 $\mu$m) are shown in height mode, with a scale of 60 nm. The inserted image in C_70 h is a SEM image of the corresponding sample.
4.3.3 Characterization of Phosphate Surface Complexes and Secondary Mineral Phases

ATR-FTIR spectra of phosphate surface complexation are shown in Figure 4.4. The spectra for 1 mM phosphate and 10 mM phosphate showed different peaks, suggesting concentration-dependent phosphate complexation with biotite. In previous studies, the peaks at 1080 and 1137 cm\(^{-1}\) were assigned to surface precipitates of AlPO\(_4\).\(^{171,179}\) From comparison with literature, the broad and weak peak at 1080 cm\(^{-1}\) in the 1 mM phosphate spectrum and the peak at 1074 cm\(^{-1}\) in the 10 mM phosphate spectrum (with slight shifts) probably resulted from the formation of surface AlPO\(_4\) precipitates. The precipitation could contribute to the lower aqueous Al concentrations observed in both the 1 mM and 10 mM phosphate systems. The peaks at 1007 cm\(^{-1}\) and 992 cm\(^{-1}\) with 1.0 mM phosphate are attributed to Fe–PO\(_4\) monodentate mononuclear complexation.\(^{170}\) More peaks were observed with 10 mM phosphate due to a mixture of surface complexes between phosphate and Al and Fe sites. The peaks at 1105 cm\(^{-1}\), 1015 cm\(^{-1}\), and 985 cm\(^{-1}\) are assigned to Al–PO\(_4\) monodentate mononuclear complexation,\(^{171}\) and peaks at 1015 cm\(^{-1}\) and 985 cm\(^{-1}\) are also assigned to Fe–PO\(_4\) monodentate mononuclear complexation.\(^{170}\) Such monodentate mononuclear surface complexation between Fe or/and Al and phosphate can promote the release of Fe and Al, subsequently enhancing the dissolution of Si and Mg.\(^{147-148,173-174,180}\) The apparently more numerous and stronger monodentate mononuclear complexes formed with 10 mM could promote biotite dissolution more significantly than 1 mM phosphate, consistent with ICP-OES results. The enhanced dissolution also could further increase the saturations of secondary minerals and enhance precipitation. There is a caveat to this conclusion, in that the ATR-FTIR analysis was conducted at room temperature and
atmospheric pressure. Therefore, the spectra may differ under high temperature and pressure. However, to minimize any potential effects, the initial pH of the ATR-FTIR experiments was adjusted to be 3.16, the same pH as in the biotite dissolution experiments. Thus, although we cannot accurately estimate the potential effects of temperature on phosphate complexation with biotite surface due to a lack of references, the dominant phosphate species in both conditions is $\text{H}_2\text{PO}_4^-$, because both have the same pH. Furthermore, the ATR-FTIR experimental observations were consistent with the promoted biotite dissolution by 10 mM phosphate. Hence, we expect the general mechanism to be the same under GCS relevant conditions.

Figure 4.4 Normalized ATR-FTIR spectra for biotite contacted with 1 mM (red solid line) and 10 mM (blue dashed line) phosphate with an ionic strength of 1.0 M and initial pH of 3.16. The spectrum of biotite contacted without phosphate in 1.0 M NaCl was used as background and subtracted from the raw spectrum.
Homogeneous precipitation in solution and heterogeneous precipitation on surfaces were observed after reaction with 1 mM and 10 mM phosphate for 22 h, as shown in Figure 4.5. The 22 h samples were chosen because we observed lower aqueous concentrations of Al\(^{3+}\) with phosphate from that time point on. Samples taken from solutions were amorphous, without obvious electron diffraction patterns observed. EDX analyses (Figure 4.6) showed that the precipitated particles were abundant in P and Fe. On the other hand, particles detached from biotite surfaces have clear lattice fringes (Figure 4.5A2). The calculated d-spacings, 1.82 Å and 2.00 Å, matched with gibbsite.\(^{164}\) Although
thermodynamically the 1 mM and 10 mM phosphate systems were not supersaturated with gibbsite after 22 h reaction (Table 4.1), gibbsite could still form due to local supersaturation near biotite surfaces, and its heterogeneous precipitation on biotite surfaces could occur at lower ion concentrations than required for homogeneous precipitation. Consistently, higher amounts of Al were observed in the particles with phosphate (Figure 4.6). Therefore, secondary mineral precipitation helped reduce aqueous Fe and Al concentrations in the 1 mM and 10 mM systems. After 96 h reaction with 10 mM phosphate, minerals abundant in P, Fe, and Al were observed on the biotite surface (Figure 4.5B and Figure 4.6). By matching the electron diffraction patterns (Table 4.2), we found that the potential secondary precipitates included strengite (FePO₄·H₂O), gibbsite (Al(OH)₃), and berlinite (AlPO₄). Although the dissolution of biotite was promoted by 10 mM phosphate, secondary precipitation reduced the aqueous Fe and Al concentrations, leading to the lower net Al and Fe concentrations observed by ICP-OES. Obvious promotion effects on biotite dissolution by 10 mM phosphate might also occur, because an excess amount of phosphate was available to remove Al and Fe cations from solution, further promoting the forward dissolution, but not in the 1 mM phosphate system.

Table 4.2 Analyses of d-spacings obtained from particles detached from biotite reacted with 10 mM phosphate for 96 h (corresponding to Figure 4.5B).

<table>
<thead>
<tr>
<th>d-spacing measured (Å)</th>
<th>d-spacing from reference for Crystal Plane</th>
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<tr>
<td></td>
<td>Strengite</td>
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<tr>
<td></td>
<td>2.51</td>
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<td></td>
<td>1.67</td>
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<td>1.48</td>
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<td>1.29</td>
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</table>
EDX analyses by HR-TEM of particles observed from samples: (1) taken from solutions after reaction for 22 h with 1 mM (A) and 10 mM (B) phosphate, and taken from biotite surface with 10 mM phosphate (C), (2) taken from biotite surface with 10 mM phosphate after 96 h reaction (D). The corresponding images are shown in **Figure 4.5**. M/Al is the Al weight percent-normalized element content. For unreacted biotite, the weight ratios of different elements are O : Fe : Si : Mg : Al = 6.5 : 2.3 : 3.1 : 1.4 : 1.0.

The residual phosphate concentrations after 96 h reaction in the 1 mM phosphate and 10 mM phosphate systems were about 0.7 mM and 9.5 mM, respectively (**Figure 4.7**). The decreases of phosphate concentrations in the reaction systems can result from both phosphate adsorption on the biotite surface and precipitation of phosphate minerals. Moreover, the phosphate concentrations obviously decreased after 44 h reaction, which is consistent with the decrease of aqueous Fe and Al concentrations due to secondary precipitation with phosphate. Therefore, with phosphate, in the first stage (0–40 h for Fe and 0–20 h for Al), dissolution was dominant; then, in the second stage (over a longer time), secondary precipitation of Fe- and Al-bearing phases was predominant over dissolution with higher mineral saturation indices (**Table 4.1**), reducing the Fe and Al concentrations.
in the solutions. To investigate how chemical reactions with phosphate alter the wettability of biotite basal surfaces, we conducted contact angle measurements under both ambient conditions and high temperature and pressure conditions.

![Residual concentrations of phosphate in the brine at various elapsed reaction times.](image)

**Figure 4.7** Residual concentrations of phosphate in the brine at various elapsed reaction times.

### 4.3.4 Enhanced Wettability of Biotite Basal Surfaces by Chemical Reaction with Phosphate

Biotite surface wettability was significantly enhanced after interactions with phosphate, as indicated by contact angles measured under ambient conditions for biotite samples reacted in control, 0.1 mM (a concentration closer to general field site conditions), 1 mM, and 10 mM phosphate at 95 °C and 102 atm CO₂ for 70 h (Figure 4.8A). For 0.1 and 1 mM phosphate samples, the contact angles were close, but both were lower than control samples. The dissolution extents for samples reacted in the control, 0.1 mM, and 1 mM phosphate systems were similar, and no significant precipitation occurred on these sample surfaces (Figure 4.8A). In other words, for these three samples, changes in the surface morphology were not discernible, with similar root-mean-square roughness values (Figure 4.8A). Therefore, we conclude that in a low phosphate concentration
systems, surface adsorption of phosphate is dominant over dissolution or secondary precipitation in enhancing the biotite surface wettability.

On the other hand, the further slight decrease of contact angles on samples reacted with 10 mM phosphate can be explained by surface precipitation. Surface roughness was much higher for 10 mM phosphate samples than for control, 0.1 mM phosphate, and 1 mM phosphate samples (Figure 4.8A). In a recent study by Zhang et al., higher surface roughness, induced by dissolution, enhanced biotite wettability. Similarly, in the present study, a secondary precipitation-induced increase of surface roughness could have also reduced the contact angle on the biotite surface, enhancing its wettability. Second, the chemical identity on the biotite surface changed because of secondary precipitation in the presence of phosphate. Hence, newly formed minerals may also affect the wettability because different minerals have their own chemical compositions, crystal structures, and surface charges (4-S6). While we could not quantitatively differentiate their roles, we can, therefore, conclude that at a high phosphate concentration both adsorption and significant secondary precipitation can contribute to the enhanced wettability.
Figure 4.8 Contact angle measurements under ambient conditions (A) and 48 °C and 102 atm CO₂ conditions (B) for reacted biotite samples under different phosphate concentrations.

4.4 Environmental Implications

In this study, for the first time, we systematically report the concentration-dependent effects of phosphate on biotite dissolution and element-specific secondary precipitation. A higher concentration of phosphate (10 mM) promoted biotite dissolution, and low concentrations of phosphate did not greatly affect biotite dissolution. However, in the presence of phosphate, even at 0.1 mM, phosphate precipitated with Fe and Al as secondary minerals both at biotite surfaces and in the aqueous solutions, reducing aqueous Fe and Al concentrations. Secondary precipitation may block pores in subsurface sites, thus reducing their porosity and permeability. Furthermore, we show the consequent surface morphology evolution and alteration of wettability of biotite under conditions relevant to subsurface sites, information which could not be obtained through simulations alone. Biotite wettability was significantly promoted by the presence of phosphate, which was
effective even in 0.1 mM phosphate and this was mainly due to phosphate adsorption. Wettability is a key factor determining the distribution and transport of fluids in subsurface sites. Therefore, the new findings about the effects of phosphate on the interfacial reactions of minerals and their subsequent physicochemical property changes can contribute to safe and efficient geologic CO$_2$ sequestration. In addition, the information about the phosphate effects can benefit our understanding of other processes where physical chemistry of phosphate is critically involved, such as other engineered subsurface processes or material fabrication.

**Acknowledgments**

We are grateful for support received from the Center for Nanoscale Controls on Geologic CO$_2$, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, via Grant DE-AC02-05CH11231. We also thank to National Science Foundation’s CAREER Award (EAR-1057117). The authors acknowledge Washington University’s Institute of Materials Science & Engineering for use of HR-TEM, and Nano Research Facility for use of SEM and ICP-OES. We also thank Prof. James Ballard for carefully reviewing our manuscript.
Supporting Information for Chapter 4

4-S1. High temperature and high pressure batch experiments

After high P/T experiments, the reactor was taken out from the heating mantle and allowed to cool. Meanwhile, the reactor was slowly degassed by releasing the pressure valve. The degassing process took about 0.5 h. Then the samples were taken out from the reactor and collected for further characterizations. The whole process was controlled to be same for different reaction conditions. The temperature decrease and degassing of CO2 should not affect the surface properties/secondary precipitate formation according to our previous studies.79,183 If releasing pressure and cooldown induced precipitation, we would not be able to observe the different evolution of surface precipitation on the 10 mM phosphate samples from other experimental conditions, such as control, and 0.1 and 1 mM phosphate systems. In addition, we used GWB to calculate mineral saturation states in the 10 mM phosphate system after 96 h reaction after degassing to ambient pressure and cooling down to 25 °C. The saturation states of secondary precipitates we observed (strengite, berlinite, gibbsite) decreased, indicating lower precipitation potential.

There is a caveat using a 0.2 µM syringe filter because it may not remove nanoscale amorphous particulates from the solution. However, we can still conclude that a higher concentration of phosphate promotes biotite dissolution and that phosphate enhances secondary precipitation of Fe- and Al-containing minerals. The formation of amorphous particulates consumed cations released from biotite dissolution, leading to lower aqueous cation concentrations. If we can successfully remove all the secondary precipitates in the solution, then the concentrations measured by ICP-OES will be the net results of dissolution and precipitation. However, if there are residual amorphous particles in the solution after filtration, the redissolution of these particles during acidification for ICP-OES sample preparation will cause higher ion concentration than the net concentrations of dissolution and precipitation, which are closer to the concentrations released from dissolution. Nevertheless, the slightly higher concentrations in ICP-OES results can still support our conclusions on the concentration-dependent and element-specific effects of phosphate.
Thermodynamic calculations:

Although, based on the calculations, illite was undersaturated, fibrous illite formed on the biotite surface in all three reaction systems. Hu et al. discussed that illite might be locally saturated near the biotite surface due to concentration and pH gradients existing between surface and bulk solution in stationary batch reactor systems. Additionally, lower ion concentrations would be required for heterogeneous nucleation of fibrous illite on a biotite surface than for the homogeneous nucleation calculated by GWB. Although the saturation ratios for gibbsite were slightly negative in the 1 mM phosphate system, it could still form on the biotite surface because of the same reasons as for illite formation. However, there is a caveat in the saturation indices obtained from GWB calculations by taking the ICP-OES results as input. The ICP-OES results show the net cation concentrations of dissolution and secondary precipitation. The calculated indices reflect the saturation states after precipitation, and thus are lower than those of the systems starting to precipitate. Nonetheless, the trends of the saturation indices in different systems with different phosphate concentrations and after different reaction times should be same.

Thermodynamic prediction for 20 µM phosphate system:

To predict mineral saturation states for 20 µM phosphate system (a commonly found phosphate concentration in field sites), GWB calculations were conducted by taking the aqueous cation concentrations obtained in the 1 mM phosphate reaction system as inputs. This assumption of cation concentrations is reasonable because in 1 mM phosphate system, the aqueous Mg and Si concentrations are essentially similar to those in the control (Figure 4.2), the concentrations of Mg and Si in the 20 µM system should be close to both in the 1 mM phosphate and control systems. In addition, the aqueous Fe and Al concentrations might be higher in 20 µM system than in 1 mM phosphate system due to the more secondary precipitation of Fe- and Al-containing minerals in a higher concentration of phosphate system. Using the cation concentrations in the 1 mM phosphate can predict the minimum mineral saturation states in the 20 µM phosphate system, indicating the precipitation potential. The calculation results are also shown in Table 4.1. Strengite is saturated with just 20 µM phosphate, indicating that even very lower phosphate concentrations can promote secondary precipitation of Fe- and Al-containing minerals. The
lower mineral saturation states with 20 µM phosphate than 1 mM and 10 mM phosphate systems could confirm our assumption that the extent of secondary precipitation is lower for 20 µM than 1 mM phosphate.

**In-situ pH measurements:**

A special pH probe (Corr Instrument, San Antonio, TX) was calibrated and used to measure in-situ pH at 95 °C and 102 atm of CO₂. The method of pH probe calibration was modified from Shao et al. The probe was calibrated at 95 °C under room pressure in 1 M NaCl solution with different pH values, adjusted under ambient conditions. Shao et al. reported that pressure within 1-102 atm does not affect the calibration. The pH of the calibration solutions at 95 °C was calculated using GWB. After recording the potentials of the pH probe at different pH solutions, a calibration curve could be obtained to link potentials with pH values at 95 °C. During pH measurements, the probe was put inside the reactor, where 25 pieces of biotite flakes were reacting in 100 mL of 1 M NaCl solution. This solid to liquid ratio was the same as in the batch dissolution experiments. The in-situ pH measured after 96 h reaction was 3.3, close to the GWB calculated pH value.

**4-S2. Contact angle measurements**

**Contact angles measured under ambient conditions:**

Under ambient conditions with DI water, using a contact angle analyzer (Surface Electro Optics, Phoenix 300), contact angles were measured for biotite samples reacted in control (A), 0.1 mM (B), 1 mM (C), and 10 mM (D) phosphate systems at 95 °C and 102 atm of CO₂ for 70 h (Figure 4.1). The absolute values of the ambient condition contact angle can be different from those obtained at high temperature and CO₂ pressure. However, based on our prior testes, the general trend of contact angles among the biotite samples reacted in different phosphate systems should be the same.

**Contact angles measured under high P/T:**

The detailed process can be found in 2-S2.
4-S3. Aqueous complexation

Aqueous solutions after reaction for 22 h in control, 0.1 mM, 1 mM, and 10 mM phosphate systems were filtered through a 0.2 µm membrane and measured by UV-Vis. Figure 4-S1 shows a peak around 275 nm for all spectra. It has been reported that both FeOH\(^{2+}\) and FeH\(_2\)PO\(_4\)\(^{2+}\) complexes contribute to the absorbance at 275 nm.\(^{184}\) The difference in absorbance from the four systems was not discernible with a low value around 0.05, indicating the FeH\(_2\)PO\(_4\)\(^{2+}\) complex amount was very small in the phosphate systems. Hence, aqueous complexation in the phosphate systems is not the main mechanism affecting biotite dissolution.

![Figure 4-S1 UV spectra of reacted solutions](image)

4-S4. Analyses of crack depth

Figure 4-S2 Average depths of cracks formed on biotite basal surfaces after reaction. The depth was taken from the average of the depths of 80 spots from four representative AFM images obtained from the reacted samples.

![Figure 4-S2 Crack Depth vs. Reaction Time](image)
4-S5. SEM measurements

**Figure 4-S3** SEM observations of biotite basal surface after reaction at 95 °C and 102 atm of CO₂ for 70 h with 10 mM phosphate. On the left is an SEM image of the reacted basal surface, and on the right are the EDX results of the particle formed with 10 mM phosphate, indicated by the white box in the left image, and unreacted biotite (SEM image not shown). M/Si is the Si weight percent-normalized element content. The white arrow in the left image points to the thin film of amorphous phases.

**Figure 4-S4** AFM contact mode images for biotite basal planes after 70 h reaction at T = 95 °C and P_{CO₂} = 102 atm with a salinity of 1.0 M NaCl and initial pH of 3.16 without phosphate (A), with 0.1 mM phosphate (B), 1 mM phosphate (C), and with 10 mM phosphate (D).
4-S6. Effects of secondary minerals on wettability alterations

Strengite, berlinite, and gibbsite were identified on the biotite surface after reaction with 10 mM phosphate. While hydrophilicity information for strengite or berlinite is not available, a previous report found that a gibbsite surface is much more hydrophilic than a siloxane surface.\(^{58}\) Therefore, if gibbsite is a secondary mineral phase, it will make the exposed surface more hydrophilic than a siloxane-terminated biotite basal surface.\(^ {154}\) Without knowing strengite or berlinite hydrophilicity information, we cannot determine whether the precipitation of different phases is the most dominant mechanism changing the surface wettability. Nevertheless, the coating of gibbsite on the biotite surface can be a factor enhancing the surface hydrophilicity.

4-S7. P removal and secondary mineral precipitation

We used biotite flakes with dimensions of 2.0 cm × 0.8 cm, so the original biotite surface area was around 3.2 cm\(^2\). After 70 h reaction, the removal of phosphate was about 0.4 mM in the 10 mM phosphate system. Because we had both homogeneous precipitation and surface precipitation, we roughly assume that 0.1 mM phosphate was removed by precipitation on the surface and that 0.05 mM strengite formed. The density of strengite is about 2.87 g/cm\(^3\). We further assumed that the thickness of surface precipitates was 200 nm, so the covered surface area would be about 130 cm\(^2\), much higher than 3.2 cm\(^2\). Therefore, more than enough phosphate was removed from solution than was needed for surface coverage. This can in turn support that there is homogeneous precipitation.

4-S8. The role of CO\(_2\)

After CO\(_2\) is injected into the system, it will dissolve into brine, forming CO\(_2\)(aq), H\(^+\), HCO\(_3^−\), and CO\(_3^{2−}\). The pH will decrease to about 3.16 in 1.0 M NaCl solution at 95 °C and 102 atm of CO\(_2\). At the low pH, the main component of dissolved species will be CO\(_2\)(aq), but the concentration of carbonate will be lower than 1e-8 molal under our experimental conditions. Our previous report\(^ {78}\) revealed that bicarbonate complexation effects on biotite dissolution were minor under the experimental conditions (1 M NaCl, 35–95 °C and 75–120 atm CO\(_2\)). However, the CO\(_2\) molecules in brine could get into the
biotite interlayer and promote biotite surface cracking. In the current study, we maintained the same temperature and pressure for all three reaction systems (control, 1 mM phosphate, and 10 mM phosphate). Therefore, the differences of the results came from the presence of different phosphate concentrations. CO₂ plays an important role in biotite dissolution but is not responsible for the different results observed for the three reaction systems.

4-S9. Formation of fibrous illite

Generally, biotite dissolves according to the following chemical equation:

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

As reported in previous publications, the local dissolved ions near the biotite surface can precipitate out as fibrous illite. Additionally, 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.

4-S10. Dissolution stoichiometry

Figure 4-S5 Normalized ion concentrations by biotite chemical formula after reactions in control (A), 1 mM phosphate (B), and 10 mM phosphate (C) system at 95 °C and 102 atm CO₂.
Chapter 5. The Effects of Phosphonate-based Scale Inhibitor on Brine–Biotite Interactions under Subsurface Conditions

The results of this chapter have been published in *Environmental Science & Technology*, 2018. DOI: 10.1021/acs.est.7b05785.

Abstract

During engineered subsurface operations, phosphonates additives are commonly used to inhibit formation of mineral scales. In addition to our findings presented in Chapters 2–4 about brine–mineral interactions with naturally existing aqueous species, the effects of added phosphonates on brine–mineral interactions can impact engineered subsurface operations. Thus, in this chapter, batch experiments of biotite dissolution (0–96 h) were conducted in solutions containing 0–1.0 mM diethylenetriaminepenta(methylene)phosphonate (DTPMP, a model scale inhibitor), at conditions simulating subsurface environments (95 °C and 102 atm CO₂). The phosphonate groups in DTPMP enhanced biotite dissolution through both aqueous and surface complexations with Fe, with more significant effects at a higher DTPMP concentration. Surface complexation made cracked biotite surface layers bend, and these layers detached at a later stage (≥ 44 h). The presence of DTPMP also promoted secondary precipitation of Fe- and Al-bearing minerals both in the solution and on the reacted biotite surfaces. With 1.0 mM DTPMP after 44 h, significant coverage of biotite surfaces by precipitates and less detachment of cracked layers blocked reactive sites and inhibited further biotite dissolution.
Furthermore, adsorption of DTPMP made the reacted biotite basal surfaces more hydrophilic, which may affect the transport of reactive fluids. This study provides new information on the impacts of phosphonates in brine–mineral interactions, benefiting safer and more environmentally sustainable design and operation of engineered subsurface processes.

5.1 Introduction

Geologic CO$_2$ sequestration (GCS) and CO$_2$-enhanced oil/gas recovery (EOR) are important engineered subsurface operations to mitigate global warming and meet energy demands.$^{1, 166, 185}$ The chemical and physical properties of rocks, such as their porosity, permeability, surface chemistry, and wettability, greatly affect the engineered operations. During these processes, scale formation of calcium carbonate, calcium sulfate, and barium sulfate is a significant problem which can reduce the porosity and permeability of reservoirs and block flow in production wells.$^{29-32}$ To prevent the formation of mineral scales, scale inhibitors have been used.$^{28}$ In the course of scale inhibitor application, interactions between rocks and minerals with the scale inhibitors determine their retention and release, thus influencing their efficacy in inhibiting scale formation. Wettability, an important rock property, largely determines the distribution and mobility of reactive fluids, such as CO$_2$ and oil/gas.$^{56, 186}$ It has been reported that mineral wettability can be altered by chemical reactions of minerals.$^{168, 187}$ Based on the known strong chelating capability of scale inhibitors and their chemical interactions with minerals, one can expect that significant brine–mineral interactions can occur during applications of scale inhibitors in subsurface operations.$^{176-177, 188-191}$ Therefore, for safer and more efficient subsurface
operations, it is important to understand how scale inhibitors interact with rocks and minerals under relevant conditions.

Phosphonates, which contain one or more functional groups (-PO$_3$H$_2$) and P-C-N-C-P or P-C-P bonds, are commonly used as scale inhibitors in engineered subsurface operations. These compounds are strong chelating agents that can complex with aqueous metal ions and metal sites at mineral surfaces, affecting mineral dissolution. It was reported that aqueous Fe (II/III) can complex strongly with phosphonate functional groups. Yan et al. observed that iron was extracted from Marcellus shale by phosphonates due to their strong chelating properties, and that a ferrous or ferric phosphonate precipitate might form. However, the identity of the reaction products and impacts of these unexpected and uncommon mineral scales on physicochemical properties of rocks were not discussed.

The reported average concentration of phosphonates in subsurface operations, such as in fracking fluids, is ~0.023 wt.% (~0.5 mM). They are applied under pressure and then work at a concentration above a minimal inhibitor concentration by affecting nucleation and growth of scale minerals. During subsurface operations, phosphonate concentrations can change due to interactions with rocks and minerals. They will also vary from near the wellbore area to areas away from the wellbore. Recent studies have reported phosphonate adsorption onto reservoir rocks at low concentrations (generally < 0.06 mM) and formation of precipitates (Ca-phosphonate or Fe-phosphonate) on mineral surfaces at higher phosphonate concentrations at 70 °C, with the concentration threshold depending on mineralogy and CO$_2$ pressures. However, information on the effects of different phosphonate concentrations on mineral dissolution and secondary precipitation is
lacking. In addition, if phosphonates precipitate as solid forms, they will reduce the available inhibitor concentrations in solution and influence their performance in scale inhibition. Thus, we need a better understanding of the effects of different concentrations of phosphonates on the chemical processes of rocks and minerals under subsurface conditions.

Shales are the main reservoirs for unconventional oil and gas recovery, led by new developments in horizontal drilling and hydraulic fracturing.\textsuperscript{10-11} They have also been evaluated as host rocks and caprocks for CO\textsubscript{2} storage.\textsuperscript{12} Shales are mixtures of various clay minerals, with fine grains of quartz, feldspars, and calcite.\textsuperscript{16} Despite the important role of shales in engineered subsurface operations, previous studies have focused only on scale inhibitor–carbonate/sandstone interactions by investigating retention and release mechanisms of phosphonates.\textsuperscript{31,195-196} Only a few studies investigated the adsorption and precipitation of scale inhibitors on shale formations,\textsuperscript{176, 197} and their effects on the dissolution of shales and on secondary precipitation still remain poorly understood. Moreover, the solubility of Fe-phosphonate mineral is many orders of magnitude lower than that of Ca-phosphonate.\textsuperscript{31, 188-189} Phosphonates may enhance secondary precipitation when they interact with Fe-bearing minerals, which can further influence mineral dissolution in subsurface sites. Although phosphonates can much differently affect the dissolution of Fe-bearing minerals and non-Fe-bearing minerals, such as sandstone or carbonate minerals, studies on Fe-bearing shale minerals are very limited.

Therefore, using biotite as a model Fe-bearing clay mineral,\textsuperscript{9, 79} this study investigated the effects of phosphonates on brine–biotite interfacial interactions and mechanisms under conditions relevant to subsurface environments (95 °C and 102 atm
CO$_2$). The results will improve our understanding of the impacts of phosphonate additives on the geochemical processes of reservoir rocks and minerals and the subsequent physicochemical property changes of mineral surfaces. The findings can provide new fundamental information that can benefit environmental safety and efficiency of engineered subsurface operations.

5.2 Experimental Section

5.2.1 Minerals and Chemicals

Biotite from Bancroft, Ontario, Canada (Ward’s Natural Science, NY) was used. The chemical composition, analyzed by X-ray fluorescence (XRF), was K$_{0.91}$Na$_{0.08}$Ca$_{0.05}$Mg$_{1.72}$Mn$_{0.06}$Fe$_{1.12}$Ti$_{0.12}$Al$_{1.00}$Si$_{2.98}$O$_{10}$(F$_{0.51}$(OH)$_{0.49}$)$_2$ (Table 2.1). Biotite flakes measuring 1.0 cm × 0.8 cm, with a thickness of 80 ± 10 µm, were prepared by cleaving specimens along the {001} basal planes. The biotite flakes were sonicated in acetone, ethanol, and isopropanol successively for 5 min each to remove organic matter, then rinsed with deionized (DI) water (resistivity ≥ 18.2 MΩ·cm, Barnstead Ultrapure Water Systems), and dried with high purity nitrogen gas. They were stored in dust-free tubes for further dissolution experiments.

Diethylenetriaminepenta(methylene)phosphonate (DTPMP, Sigma-Aldrich) was used as a model phosphonate scale inhibitor. To mimic the water chemistry in subsurface environments, reaction solutions of 0 (control), 0.05, 0.5 (the reported average site value), and 1.0 mM DTPMP were prepared, all with a salinity of 0.5 M NaCl.
5.2.2 High Temperature and High Pressure Reaction Systems

The temperature and pressure of engineered subsurface sites are generally in the ranges of 35–110 °C and 73.6–600 atm, respectively.\textsuperscript{44, 80, 140} Biotite dissolution experiments were conducted at 95 °C and 102 atm CO\textsubscript{2}, simulating CO\textsubscript{2}-involved GCS and EOR operation conditions. A benchtop reactor was used for the reaction, as described in our previous studies (Figure 2.1).\textsuperscript{79, 168} The relatively high temperature was used to accelerate the reactions and make experimental observations available within reasonable time frames, and to compare them with previous studies.\textsuperscript{9, 79, 168, 187} To control the initial pH values within a small range, the solutions of four different DTPMP concentrations were adjusted to pH 5.6 with diluted hydrochloric acid (HCl) under ambient conditions. Measured by a pH probe (Corr Instruments, TX) that can work under 20–120 °C and 1–136 atm, the initial \textit{in situ} pH values for all four solutions were within a small range of 3.0–3.4 at 95 °C and 102 atm CO\textsubscript{2}. The section 4-S1 in the Supporting Information for Chapter 4 gives detailed information about \textit{in situ} pH measurements. Triplicate PTFE tubes containing 4 mL of the prepared solutions and a piece of clean biotite flake were placed in a 300 mL reactor. To mimic and investigate the effects of DTPMP on brine–biotite interactions in the early period of injection, at six elapsed times between 0–96 hours, the reactor was cooled and slowly degassed, both within 30 min.

5.2.3 Analyses of Aqueous Samples

After degassing, the solutions were filtered through 0.2 µm polypropylene membranes and then analyzed by ultraviolet-visible spectroscopy (UV-Vis, Thermo Scientific Evolution 60S) in the 200–500 nm wavelength range for aqueous complexes.
Then, the solutions were acidified in 1% trace metal nitric acid (HNO₃) to quantify the concentrations of dissolved aqueous cations and total phosphorus using inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 7300 DV). The aqueous phosphate concentrations, which can be released by decomposition of DTPMP, were measured with ion chromatography (IC, Thermo Scientific Dionex ICS-1600).

5.2.4 Surface Characterization and Secondary Mineral Identification

The reacted biotite flakes were gently rinsed with DI water and dried with nitrogen gas, and then analyzed for surface morphology and secondary mineral phases. The surface morphology of biotite flakes was analyzed in contact mode with atomic force microscopy (AFM, Nanoscope V Multimode SPS, Veeco) under ambient conditions. Using nonconductive silicon nitride probe (tip radius of 10 nm, DNP-S10, Bruker) at a rate of 0.999 Hz and with a deflection set point of 1.975 V, we scanned areas of 50 µm × 50 µm. The obtained AFM images were analyzed with Nanoscope software (v7.20).

Scanning electron microscopy (SEM, Nova NanoSEM 230) was used to analyze both the reacted biotite basal surfaces and the particles in the solutions. A 10.00 kV electron accelerating voltage was used for imaging. To capture possible detached biotite layers and any particles formed in the solutions, after the dissolution reactions, the polypropylene membranes used for filtration were washed with DI water and examined by SEM. SEM images were taken and energy dispersive X-ray spectroscopy (EDX) was used to analyze the elemental compositions of the particles.
High resolution-transmission electron microscopy (HR-TEM, JEOL-2100F) characterized the secondary mineral phases. To examine particles formed in solutions, TEM samples were prepared in the following way: after reaction for 70 h, the solutions were centrifuged at 5000 rpm for 5 min. The particles in the bottom were collected, 40 mL of DI water was added, and the suspension was centrifuged again. This process was repeated for 5 times to remove ionic species and prevent unexpected precipitation during sample drying. After centrifugation, a droplet from the bottom of the solution (containing only particles formed during the reactions) was placed on a Formvar/carbon coated-Cu grid (Electron Microscopy Science, PA) and allowed to dry. To examine particles formed on the reacted biotite surfaces, TEM samples were prepared by sonicating the reacted biotite flake in ethanol for 5 min, detaching particles from the surface into ethanol, and placing a droplet of the suspension on a TEM grid. Lattice fringes and electron diffraction patterns were obtained to identify the secondary mineral phases. Elemental compositions were also analyzed by energy dispersive X-ray spectroscopy during the TEM measurements.

5.2.5 Contact Angle Measurements

Under ambient conditions, biotite flakes reacted at 95 °C and 102 atm CO₂ were analyzed for contact angles using a contact angle analyzer (Surface Electro Optics, Phoenix 300). A droplet of DI water was generated by a syringe needle, placed on the biotite basal surface, and imaged. Contact angles were then obtained by analyzing the images (Figure 4.1A). Six measurements were made on every biotite sample, and the average contact angles were reported.
5.3 Results and Discussion

5.3.1 DTPMP Promoted the Dissolution of Biotite

The effects of DTPMP on the evolution of aqueous cation concentrations varied for different cations after biotite reacted under high temperature and high pressure conditions. The release of interlayer K, mediated by ion-exchange reactions, from biotite was not affected by the presence of DTPMP (Figure 5.1). Due to the controlled background salinity and initial pH (Table 5.1), similar extents of ion-exchange reactions between interlayer K and cations in the reaction solutions occurred at all DTMPM concentrations. However, the aqueous concentrations of framework cations (Si, Mg, Fe, and Al) were dependent on DTPMP (Figure 5.1). The Si and Mg concentrations were higher with DTPMP than in control experiments without DTPMP, indicating the promotion of biotite dissolution by DTPMP. On the other hand, we observed that aqueous concentrations of Fe and Al were lower with DTPMP than those in control experiments, especially after longer reaction times (≥ 44 h). Note that the aqueous concentrations measured by ICP-OES are the net results of biotite dissolution and secondary mineral precipitation. Fe- and Al-bearing phosphonate/phosphate minerals are quite insoluble, with solubility product constants (K_{sp}) lower than the order of 10^{-19}. Therefore, we hypothesized that DTPMP could promote biotite dissolution and the release of Fe and Al. Secondary precipitation of Fe- or Al-bearing minerals then consumed Fe and Al released during biotite dissolution, resulting in their lower aqueous concentrations as measured by ICP-OES.

Table 5.1 In situ pH at 95 °C with different DTPMP concentrations.
The effects of DTPMP on the evolution of framework cations were also dependent on DTPMP concentrations. For Si and Mg, which were assumed not to have significant secondary precipitation, their aqueous concentrations increased with increasing DTPMP concentrations from 0 to 0.5 mM. Interestingly, however, the Si and Mg concentrations in 1.0 mM DTPMP reaction system were lower than those in the 0.5 mM DTPMP systems. Because the initial and final pH values of the control and 1.0 mM DTPMP systems were close (Table 5.1), the pH difference might not influence biotite dissolution and secondary precipitation. To explain the observations, several possible scenarios can be considered: First, aqueous complexation and surface complexation could affect biotite dissolution. With increasing DTPMP concentration, more significant aqueous complexation could increase the apparent solubility of minerals, thus promoting biotite dissolution. DTPMP adsorption onto biotite surfaces could either promote or inhibit dissolution by forming different configurations of mono/bi/multi-dentate mono/bi/multi-nuclear surface complexation. Second, more promoted dissolution and even more significant secondary precipitation with 1.0 mM DTPMP could result in the lower net aqueous concentrations. Third, if the secondary precipitation occurred on the biotite surface, the precipitates might block reactive surface sites and even inhibit further dissolution of biotite. To evaluate these three possible mechanisms, further studies were conducted.

<table>
<thead>
<tr>
<th>Experimental Condition</th>
<th>Initial pH</th>
<th>96 h reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>3.01</td>
<td>3.28</td>
</tr>
<tr>
<td>0.05 mM</td>
<td>3.10</td>
<td>N/A</td>
</tr>
<tr>
<td>0.5 mM</td>
<td>3.23</td>
<td>N/A</td>
</tr>
<tr>
<td>1.0 mM</td>
<td>3.42</td>
<td>3.44</td>
</tr>
</tbody>
</table>
Figure 5.1 Effects of DTPMP concentrations (0, 0.05, 0.5, and 1.0 mM) on the evolution of aqueous cation concentrations of K, Si, Al, Mg, and Fe during biotite dissolution with an ionic strength of 0.5 M NaCl at 95 °C and 102 atm of CO₂. Error bars are the standard deviation of triplicate experiments.

5.3.2 Aqueous Complexation of DTPMP with Ferric Ions (Fe(III))

UV-Vis analyses of the reacted solutions after filtration were conducted to characterize aqueous complexation, and the results are shown in Figure 5.2 and 5-S1. As reported by Matthijs et al., the maximum absorbance around 260 nm (Figure 5-S1) observed in this study corresponded to Fe(III)-DTPMP aqueous complexes. The UV-Vis analyses showed increasing absorbance by Fe(III)-DTPMP aqueous complexes with increasing DTPMP concentrations (Figure 5.2A). In the 0.05 mM DTPMP system, although we observed higher aqueous Fe concentrations in the ICP-OES results than in the 0.5 mM and 1.0 mM DTPMP systems (Figure 1), the aqueous Fe was not fully complexed because of the low DTPMP concentration, showing lower absorbance in the UV results.
Therefore, aqueous complexation contributed to enhancing biotite dissolution, and more significant promotion effects occurred at higher DTPMP concentrations. The observation for DTPMP effects was different from the effects of phosphate ions on biotite dissolution, where aqueous complexation was quite weak. The difference could have resulted from the higher chelating capacity of DTPMP, with several phosphonate functional groups. As the reaction continued, the absorbance decreased with time from 22 h to 44 h, indicating a decreasing aqueous complexation. The decreasing could result from lower aqueous Fe or DTPMP concentrations caused by secondary precipitation or DTPMP adsorption.

![A. Aqueous complexation](image1.png)

**Figure 5.2 (A)** UV-Vis absorbance (wavelength = 260 nm) of filtered solutions and (B) analyses of P removal after reaction with different concentrations of DTPMP (0.05, 0.5, and 1.0 mM) at 95 °C and 102 atm of CO₂.

### 5.3.3 DTPMP Promoted Secondary Precipitation and Altered Biotite Surface Morphology

The morphological evolution of the reacted biotite basal surface was dependent on DTPMP concentrations, as shown in the AFM images in Figure 5.3. Compared with control samples, increasing the concentration of DTPMP promoted the formation of cracks (red to dark channels, indicated by arrows in Figure 5.3) and increased the crack depth.
Based on analyses of 12 regions of cracks from triplicate samples after 8 h reaction, the crack depths reach to around 13 nm for the 0.5 mM DTPMP sample and 30 nm for the 1.0 mM DTPMP sample. This observation indicates that 1.0 mM DTPMP promoted more biotite dissolution at early reaction times than 0.5 mM DTPMP, consistent with UV-Vis analyses. Fibrous precipitates, identified as illite in previous studies, were formed on all four biotite samples after 3 h reaction (yellow to pink fibers, indicated by arrows in Figure 5.3). Then, rough biotite basal surfaces were observed for 0.05 mM, 0.5 mM, and 1.0 mM DTPMP samples after 8 h, 22 h, and 44 h, respectively, resulting from enhanced surface precipitation of fragile particles by the presence of DTPMP. The first occurrence of significant surface precipitation was increasingly delayed as the DTPMP concentrations increased from 0.05 mM to 1.0 mM. This delay would have resulted from enhanced biotite dissolution by more significant aqueous complexation at higher DTPMP concentrations (Figure 5.2A), which could have led to more homogeneous precipitation in the solutions than surface precipitation. At the early reaction times (< 44 h), enhanced biotite dissolution at higher DTPMP concentrations released more cations into the solutions, causing higher mineral saturations and favoring homogeneous precipitation over heterogeneous precipitation on the mineral surfaces. Notably, in the 1.0 mM DTPMP system, the greater homogeneous precipitation in the solution even led to lower aqueous cation concentrations than those in the 0.5 mM DTPMP system. In addition, Therefore, the removed aqueous P concentrations in the DTPMP systems over time were monitored by ICP-OES, and the results are shown in Figure 5.2B. At the early times (< 44 h), P removal in the 1.0 mM DTPMP system was higher than that in the 0.5 mM DTPMP system. The P was mainly removed by adsorption onto mineral surfaces or secondary precipitation.
Although we could not deconvolute the relative amounts of P removed by adsorption and secondary precipitation, the evolution of aqueous P removal hinted at more secondary precipitation in the 1.0 mM DTPMP system at an early time. This observation was consistent with a recent report that a higher phytate (an organic phosphate) concentration promoted more secondary precipitation. We initially assumed that there was no significant secondary precipitation of Si and Mg, however, the formation of Fe- or Al-bearing minerals could incorporate Si and Mg, and coprecipitation lowered the aqueous Si and Mg concentrations.

Figure 5.3 (A) Height mode AFM images of biotite basal surfaces after reaction in 0.5 M NaCl solution at 95 °C and 102 atm of CO₂ without DTPMP (Control), with (B) 0.05, (C) 0.5, and (D) 1.0 mM DTPMP. The AFM images are 50 μm × 50 μm. The height scale is 60 nm for images A3-96 h, B3-44 h, C3-22 h, and D3-22 h, and is 200 nm for the other images. The color scale from dark to pink indicates height from low to high. The different height scales were used to show the results more clearly.
On the 0.05 mM and 0.5 mM DTPMP samples, after longer reaction times \((\geq 44\) h), new layers on biotite surface were exposed due to detachment of the cracked biotite surface layers together with secondary precipitation. The surfaces of 1.0 mM DTPMP samples were significantly covered by secondary minerals. Because AFM tips are sensitive to rough surfaces, to observe the features of reacted biotite surfaces, SEM measurements were conducted for samples after 70 h reaction. In the SEM images (Figure 5.4), cracks were observed on the surfaces of all four samples. Interestingly, some cracked layers were peeled outwards from the DTPMP samples (indicated by the yellow dotted circles in Figure 5.4). Differently, in Chapter 4 of the promotion effects of inorganic phosphate on biotite dissolution, bent surface layers were not observed, probably because inorganic phosphate has a smaller molecular size than DTPMP. Phosphorus in EDX was observed on the cracked biotite layer (Figure 5-S2A), suggesting surface complexation and adsorption of DTPMP. Therefore, although reference information about DTPMP complexation with Fe or Al sites is not available to determine the configuration of surface complexation by FTIR (Fourier-transform infrared spectroscopy), it is clear that the adsorption of the large DTPMP molecules helped create the cracks and resulted in the bent layers, both of which exposed reactive surface sites and contributed to promoting the biotite dissolution. The bent cracked layers detached from the reacted biotite basal surfaces, and obviously, the 0.5 mM DTPMP sample showed the newly exposed layer and the remaining cracked layers. For the 1.0 mM DTPMP sample, the peeling was not as significant as for the 0.5 mM DTPMP samples. After 44 h reaction, the high coverage of the attacked biotite layer, together with DTPMP coating and secondary precipitation on the surface of 1.0 mM
DTPMP sample, could block the reactive surface sites and inhibit further biotite dissolution, leading to lower aqueous cation concentrations than those in the 0.5 mM DTPMP system.

<table>
<thead>
<tr>
<th>Control</th>
<th>0.05 mM DTPMP</th>
<th>0.5 mM DTPMP</th>
<th>1.0 mM DTPMP</th>
</tr>
</thead>
</table>

**Figure 5.4** SEM images of biotite basal surfaces after 70 h reaction with different DTPMP concentrations (0, 0.05, 0.5, 1.0 mM) at 95 °C and 102 atm of CO$_2$. The yellow dotted circles indicate bent cracked layers after dissolution.

### 5.3.4 Identification of Secondary Minerals

The lower aqueous Fe and Al concentrations in the DTPMP systems were hypothesized to be caused by both homogeneous precipitation in the reaction solution and heterogeneous precipitation of Fe- and Al-bearing minerals on the biotite surfaces. The hypothesis was supported by both ICP and AFM observations. To further identify the compositions and phases of the secondary minerals, SEM and TEM measurements were conducted for samples collected after 44 and 70 h reaction.

After 44 h of reaction, homogeneous precipitates were observed in the DTPMP reaction solutions (**Figure 5.5A**). The porous substrate shown in **Figure 5.5A** is the membrane used for filtration. The filtration results showed that homogeneous precipitation was more significant in the 1.0 mM DTPMP solution than in the 0.5 mM DTPMP solution. The precipitates contained mainly Fe, Al, and P as well as incorporations of Mg and Si as revealed by EDX measurements (**Figures 5-S2B**). Therefore, at this early reaction time of 44 h, the more significant homogeneous precipitation of Fe-, Al-, Mg-, Si-, and P-bearing
minerals could contribute to the lower aqueous cation concentrations observed in the 1.0 mM DTPMP system than 0.5 mM DTPMP system (Figure 5.1). The aqueous concentrations of Si and Mg were lower in the 1.0 mM DTPMP system than 0.5 mM DTPMP system, but the aqueous Fe and Al concentrations were similar between the two systems. This observation could result from the preferential release of Fe and Al over Si and Mg by complexation with DTPMP. DTPMP could strongly interact with Fe and Al, leading to higher promotion effect of Fe and Al dissolution and secondary precipitation. Note that the ICP-OES results in Figure 5.1 show net concentrations of dissolution and secondary precipitation. Considering the disproportional DTPMP promotion effects on releases of different elements and secondary precipitation, it is reasonable that the evolutions of aqueous Si and Mg concentrations were different from those of Fe and Al in the 0.5 mM DTPMP and 1.0 mM DTPMP systems.

Regarding particles in the solution, in the control system, flakes (Figure 5.5B1) were observed with a composition similar to biotite, measured by EDX (Figure 5-S2C). The porous substrate shown in Figure 5.5A1 is the membrane used for filtration. In the 0.5 mM DTPMP solution, more flakes with a similar biotite composition at a size around 10 µm were observed. The flakes were probably detached from the biotite surfaces during the reactions. Phosphorus was also identified by EDX measurements in the flakes (Figure 5-S2C), which further supports the assumption of DTPMP adsorption onto biotite surfaces. In addition to the flakes, abundant particles of several hundred nanometers were formed in the 0.5 mM DTPMP solution (Figure 5.5B1). The EDX measurements of the particles formed in solution showed they contained high amounts of P, Fe, and Al, with incorporation of Si and Mg (Figure 5-S2C). In TEM measurements, no obvious electron
diffractions were observed for those particles (Figure 5.5B2) formed in the 0.5 mM DTPMP solution, indicating amorphous phases of the secondary particles.

Figure 5.5  (A) SEM measurements of samples collected on membranes after filtering solutions reacted for 44 h at 95 °C and 102 atm of CO₂ for 70 h. (B1) SEM measurements of samples collected on membranes after filtering solutions, and (B2) TEM measurements of particles from solutions collected by centrifuge, after reaction at 95 °C and 102 atm of CO₂ for 70 h. (C) TEM image (left) and electron diffraction pattern (right) of particles formed on biotite surfaces after reaction with 0.5 mM DTPMP at 95 °C and 102 atm of CO₂ for 70 h.
On the other hand, the particles formed on biotite surfaces after reaction with 0.5 mM DTPMP were crystalized, showing strong electron diffraction patterns (Figure 5.5C). The particles were also abundant in P, Fe, and Al (Figure 5-S2A). The d-spacings calculated from the electron diffraction patterns and the lattice fringes are shown in Figure 5.6. Initially, it was anticipated that Fe- or Al-DTPMP minerals formed on biotite surfaces during the reactions because they have quite low solubility. No references for d-spacings of Fe- and Al-DTPMP minerals are available. However, by comparing the measured d-spacings with available reference information for Fe- or Al- inorganic phosphate or (hydr)oxide minerals, we can suggest that the secondary phases probably contained a mixture of minerals, including strengite (FePO₄), gibbsite (Al(OH)₃), and berlinite (AlPO₄). Furthermore, there was no d-spacing which did not match these three mineral phases. The formation of the phosphate minerals is interesting, but it is plausible because we observed up to 2.8 mM of phosphate as a degradation product of DTPMP, based on IC measurements of solutions in the DTPMP systems after high temperature and pressure experiments (Figure 5-S3). While the degradation mechanism of DTPMP is not the focus of the present study, it has been reported previously that photodegradation of phosphonates or nonilluminated degradation of phosphonates in the presence of transition metals and molecular oxygen can release phosphate. Hence, the strengite and berlinite we found could have formed from precipitation of released Fe and Al with phosphate. DTPMP could also serve as an organic template, mediating the formation of these crystalized secondary precipitates. Nonetheless, amorphous Fe- or Al-DTPMP minerals could still form on biotite surfaces, which do not have obvious electron diffraction patterns. Thermodynamic calculations for saturations of the secondary minerals were not
possible in the DTPMP systems because detailed thermodynamic data for DTPMP is not available and phosphonate can strongly affect the apparent solubility by strong complexation with cations and protons.

Figure 5.6 Top: Lattice fringes obtained during TEM measurement from particles formed on biotite surfaces after reaction with 0.5 mM DTPMP for 70 h under 95 °C and 102 atm CO₂. Bottom: Analyses of d-spacings obtained from the corresponding particles using reference. The d-spacings of 2.04 Å (2.05 Å) and 1.86 Å obtained from lattice fringes were a little different from those of 2.09 Å and 1.79 Å obtained through electron diffraction pattern, but they were within small ranges.

In summary, aqueous complexation and surface adsorption of DTPMP promoted biotite dissolution, with more significant effects at higher DTPMP concentrations.
Moreover, the enhanced formation of Fe- and Al-bearing secondary minerals in the DTPMP systems significantly consumed the released Fe and Al from biotite dissolution, resulting in lower aqueous Fe and Al concentrations. However, based on the current experimental results, we could not determine the extents of homogeneous precipitation and heterogeneous precipitation and their relative contributions to the lower aqueous Fe and Al concentrations. In the 1.0 mM DTPMP system, significant precipitation in the solution at early reaction times (< 44 h) and inhibited dissolution by surface precipitation at longer reaction times (≥ 44 h) occurred, leading to lower aqueous cation concentrations than those in the 0.5 mM DTPMP system.

5.3.5 DTPMP Enhanced Biotite Wettability

Wettability is an important parameter controlling the flow and distribution of fluids during subsurface operations. The presence of DTPMP significantly affected biotite wettability, given by contact angle, as shown in Figure 5.6. Even after just 3 h reaction, lower contact angles (around 11º) were observed for biotite samples after reaction with DTPMP than those for control samples (25º–28º) (Figure 5.7), indicating that DTPMP enhanced biotite wettability. In our recent study,168 we found that increased roughness, more negatively charged surfaces, and higher densities of hydroxyl groups on biotite surfaces induced by dissolution can contribute to enhancing biotite wettability. From the ICP and AFM results, after 3 h reaction, the reaction extents for all four samples were similar, without significant differences in released cation concentrations and surface morphology changes. Therefore, the current study shows that dissolution-induced changes in surface roughness, surface charges, and hydroxyl groups were not the main mechanisms leading to the enhanced wettability by DTPMP.
Figure 5.7 Wettability, indicated by contact angle, of biotite basal surfaces after reaction with different DTPMP concentrations (0, 0.05, 0.5, 1.0 mM) over time. The error bars are standard deviations of six measurements from triplicate experiments.

In addition, the contact angles were close for all the DTPMP samples and they did not change over time despite the significant differences in surface morphology after reaction times longer than 3 h. The observation further rules out the contribution of surface roughness to changes in surface wettability in this study. We considered that adsorption of DTPMP contributed the most to the enhanced wettability of biotite samples in the DTPMP systems. As discussed in our previous study, oxalate preferentially forms complexes with biotite edge surface sites. By analogy, DTPMP, a strong chelating agent, probably adsorbed onto edge surface sites. However, due to biotite dissolution, cracks were formed, exposing edge sites on biotite basal planes. Therefore, DTPMP adsorption could also occur on edges created by cracks in biotite basal surfaces. The adsorption of DTPMP onto the biotite surface could expose abundant hydrophilic groups (-OH) of DTPMP, thus favoring water spreading on the biotite surface and enhancing the wettability. In a recent study, phosphate adsorption and secondary precipitation induced by phosphate were reported to enhance biotite wettability, with a contact angle of around 14º for a 0.1 mM phosphate
sample. In our experimental systems, phosphate was observed in the DTPMP systems after the high temperature and high pressure reactions (Figure 5-S3). Although phosphate could also contribute to enhancing biotite wettability, we think that DTPMP adsorption was the main factor. Only a very low phosphate concentration was observed in the 0.05 mM DTPMP system (about 40 µM phosphate), and the contact angles for DTPMP samples (around 11°) were lower than phosphate samples (around 14°). However, there is a caveat that contact angles lower than 10° could not be accurately measured because the water droplet spread fully on biotite basal surface and it was difficult to distinguish the droplet and analyze the angles. In systems with different DTPMP concentrations, we might expect lower contact angles for samples reacted with higher DTPMP concentrations, due to potentially higher adsorption. Nonetheless, the limitation on contact angle measurement would make it difficult to resolve the difference. However, the main thesis, that DTPMP enhanced wettability, is still valid.

5.4 Environmental Implications

In this study, we report the roles of DTPMP in brine–biotite interactions under subsurface conditions, and their effects on the consequent surface morphology evolution and wettability alteration. The new findings will help better predict the fate and transport of scale inhibitors in subsurface environments. Furthermore, they can benefit our understanding of the porosity, permeability, and wettability changes of reservoirs and caprocks, affected by the application of scale inhibitors in engineered subsurface operations.
The mechanisms by which DTPMP promotes mineral dissolution are different from those of short-chain carboxylic acids and inorganic phosphate. As reported in previous studies, short-chain carboxylic acids and inorganic phosphate promote mineral dissolution mainly by forming surface complexation, and aqueous complexation was very weak in those systems.\textsuperscript{79,206} However, DTPMP, with five phosphonate functional groups, promoted biotite dissolution through both strong aqueous and surface complexation, with more pronounced effects at increasing concentrations (0–1.0 mM). In addition, we also observed that DTPMP altered the surface morphology of reacted biotite samples, with bent cracked surface regions, which were not observed with inorganic phosphate, and that the cracked layers detached from biotite surfaces into the reaction solutions. Similar to inorganic phosphate, however, DTPMP promoted significant homogeneous and heterogeneous precipitation of Fe- and Al-bearing minerals. These secondary minerals are unexpected scaling minerals, and are different from commonly considered scales, such as CaCO\textsubscript{3} or BaSO\textsubscript{4}. The newly formed precipitates and detached cracked surface layers may clog nano- and micro-sized pores,\textsuperscript{207} reducing the permeability or porosity of rocks.\textsuperscript{106} There is a need to deal with the unexpected precipitates induced by scale inhibitors during subsurface operations.

Wettability is a key factor affecting the transport and distribution of subsurface fluids. The enhanced mineral wettability by DTPMP may favor mineral’s contact with water, promoting the flow of non-wetting phases, such as oil/gas and supercritical CO\textsubscript{2}. The surface adsorption, secondary precipitation, and degradation of DTPMP could reduce its available concentration in the aqueous solution, which may further affect its scale inhibition performance when applied in subsurface environments.
Acknowledgments

This work was supported by the Center for Nanoscale Controls on Geologic CO₂, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, via Grant DE-AC02-05CH11231. We also thank National Science Foundation’s CAREER Award (EAR-1057117). The authors acknowledge Washington University’s Institute of Materials Science & Engineering for use of HR-TEM, and the Nano Research Facility for use of SEM and ICP-OES. We also thank Prof. James Ballard for carefully reviewing our manuscript.
Supporting Information for Chapter 5

5-S1. UV-Vis analyses

![UV-Vis analyses of filtered solutions after reaction with different DTPMP concentrations at 95 °C and 102 atm of CO₂.](image)

**Figure 5-S1** UV-Vis analyses of filtered solutions after reaction with different DTPMP concentrations at 95 °C and 102 atm of CO₂.

We reported absorbance of the aqueous complexes in this study, because a calibration curve could not be made to link absorbance and Fe-DTPMP concentration. If we mixed certain amount of DTPMP with aqueous Fe, there would be three Fe species, including Fe-DTPMP aqueous complexes, Fe-DTPMP precipitates, and Fe species not associated with DTPMP. We could measure the absorbance, but we could not know the concentration of Fe-DTPMP complexes to obtain the calibration curve. In other words, the Fe complexes are not the only aqueous Fe species. As we observed in the ICP and UV results, although ICP shows the highest Fe concentrations in the 0.05 mM DTPMP system, the aqueous Fe was not fully complexed by DTPMP because of the low DTPMP concentration, showing lower absorbance in the UV results. Therefore, the ICP and UV results showed different dependence on the DTPMP concentration.
5-S2. SEM measurements

**A. 70 h, 0.5 mM DTPMP, on surface**

![SEM measurement and EDX results of particles detached from biotite surface after reaction with 0.5 mM DTPMP for 70 h under 95 °C and 102 atm CO₂. The substrate is a Cu TEM grid.](image)

**B. 44 h, in solution**

![EDX results of particles collected from reacted solutions in control and 0.5 mM DTPMP after 70 h reaction. M/Al indicates the atomic ratio of M (Fe, Mg, Si, P, and Al) to Al.](image)

**C. 70 h, in solution**

![Figure 5-S2 A. SEM measurement and EDX results of particles detached from biotite surface after reaction with 0.5 mM DTPMP for 70 h under 95 °C and 102 atm CO₂. The substrate is a Cu TEM grid. B. EDX results of particles collected from reacted solutions in control and 0.5 mM DTPMP after 70 h reaction. M/Al indicates the atomic ratio of M (Fe, Mg, Si, P, and Al) to Al.](image)
5-S3. Evolution of phosphate concentrations

Figure 5-S3 Concentrations of phosphate released after reactions at different elapsed times in the DTPMP systems under 95 °C and 102 atm CO₂.
Chapter 6. Effects of Phosphonate Structures on Brine–Biotite Interactions under Subsurface Relevant Conditions

Abstract

Various phosphonates with different numbers of phosphonate functional groups have been used in engineered subsurface operations. However, information about commonly used phosphonate–shale interactions is limited. In this chapter, using Fe-bearing mica (biotite) as a model phyllosilicate mineral, the effects of three common phosphonates, namely IDMP (iminodi(methylene)phosphonate), NTMP (nitrilotris(methylene)phosphonate), and DTPMP (diethylenetriaminepenta(methylene)phosphonate), were studied at 95 °C and 102 atm of CO₂. During the experiments (0–70 h), IDMP remained stable, while NTMP and DTPMP were degraded and released phosphate, formate, and new phosphonates with smaller molecular weights. Due to the differences in chelating capability affected by structure, IDMP, with the fewest phosphonate functional groups, promoted biotite dissolution mainly through surface complexation, and DTPMP, containing the most functional groups, promoted biotite dissolution mainly through aqueous complexation. The presence of phosphonates enhanced secondary precipitation of P, Fe, and Al-bearing minerals, and their phosphonate structures affected the morphologies, phases, and distributions of secondary precipitates. As a result of phosphonate–biotite interactions (mainly due to surface adsorption), the biotite surfaces became much more hydrophilic. This study
provides new insight into structure-dependent phosphonate–mineral interactions, and the results have important implications for the safety and efficiency of energy-related subsurface operations.

6.1 Introduction

Phosphonates are widely used as scale inhibitors in a variety of technical and industrial applications, such as cooling water systems, textile production, and subsurface oil/gas recovery. In particular, during unconventional oil/gas recovery from shale reservoirs led by horizontal drilling and hydraulic fracturing, phosphonates have been used to inhibit mineral scale formation that can reduce the porosity and permeability of the fractured rocks. The average concentrations of scale inhibitors in fracking fluids are around 0.023% by weight percent (~0.5 mM). To ensure effective scale inhibition, phosphonates need to be used in concentrations higher than threshold concentrations. However, it has been reported that phosphonates could have strong chemical reactions with mineral surfaces, resulting in significant mass loss in solutions and affecting the performance of scale inhibition. Moreover, phyllosilicates are abundant minerals in shale reservoirs, which are the main subsurface reservoirs for unconventional oil and gas recovery. Thus, phosphonate–phyllosilicate interactions can affect available phosphonate concentrations in the solution, or they can also impact the physico-chemical properties of phyllosilicates. Therefore, it is important to understand the interactions between phosphonates and phyllosilicate minerals.

Phosphonates contain C-P and/or C-N bonds and usually have more than one phosphonate functional group (\(-\text{PO}_3\text{H}_2\)). A wide range of phosphonates with various
numbers of phosphonate functional groups has been used in oil/gas production fields. So far, the adsorption of phosphonates onto mineral surfaces and their secondary mineral precipitation have been investigated. The adsorption depends on phosphonate structure, concentration, pH, temperature, and mineralogy. For example, the adsorption and complexation of phosphonates onto goethite surfaces is related to their structure, and phosphonate adsorption decreases as the number of phosphonate functional groups increases. However, the effects of phosphonate surface adsorption on mineral dissolution are still unclear. In addition, phosphonates are strong chelating agents that can form aqueous complexes with metal ions, with the chelating ability depending on the number of functional groups. Aqueous complexation can in turn promote mineral dissolution by reducing the apparent saturation in solution and increasing the mineral’s solubility. Considering both surface adsorption and aqueous complexation, the structures of phosphonates may affect mineral dissolution and subsequent secondary mineral precipitation. However, information on the relationship between phosphonate structure and mineral dissolution and precipitation is limited.

The chemical stability of phosphonates affects their scale inhibition performance. Under ambient conditions, structure-dependent degradation of phosphonates has been reported. Under subsurface relevant conditions (e.g., high temperature and pressure, limited oxygen, and darkness), we have investigated the degradation of DTPMP, a phosphonate containing five phosphonate functional groups, and found that the degradation was induced by reactive oxygen species generated through oxygenation of biotite. However, the degradation of phosphonates with different structures has not been investigated under relevant conditions. Further, phosphonate degradation can change an
original structure by releasing phosphate and formate to form a new phosphonate. Then, the newly formed phosphonate and phosphate ions may affect mineral dissolution and secondary precipitation in a different way. Hence, the chemical stability of phosphonates may also affect phosphonate–mineral interactions.

Chemical reactions of minerals are known to alter their surface wettability, which is an important parameter controlling the distribution and transport of reactive fluids at subsurface sites. The adsorption of phosphonates with different structures, and the mineral dissolution and subsequent surface precipitation may further affect mineral wettability. To better understand the impacts of phosphonate applications at subsurface sites, we also need to investigate the consequent wettability alterations of minerals by phosphonate reactions.

Therefore, the goal of this study was to examine the interactions between phosphonates with different numbers of phosphonate functional groups and biotite, a model phyllosilicate mineral, under subsurface relevant conditions (95 °C and 102 atm of CO₂). The chemical stability of phosphonates, biotite dissolution, secondary mineral precipitation, and mineral wettability alteration were characterized. Then, the mechanisms of phosphonate–biotite interactions were further elucidated by considering phosphonate structure-dependent degradation, surface complexation, aqueous complexation, and extents of secondary precipitation. The new findings from this study will benefit our understanding of the impacts of different phosphonates on the geochemical reactions of minerals and the subsequent wettability alteration by their interactions. The information can help evaluate the applications of phosphonates with different structures and choose more appropriate phosphonates for scale inhibition.
6.2 Experimental Section

6.2.1 Mineral and Chemicals

Biotite, purchased from Ward’s Natural Science, had an elemental composition of K_{0.91}Na_{0.08}Ca_{0.05}Mg_{1.72}Mn_{0.06}Fe_{1.12}Ti_{0.12}Al_{1.00}Si_{2.98}O_{10}(F_{0.51}(OH)_{0.49})_{2}, as characterized by X-ray fluorescence. Biotite flakes were prepared by cleaving along the {001} basal planes and cutting them into 1.0 cm × 0.8 cm rectangles with a thickness of 80 ± 10 µm. The flakes were sonicated in acetone, ethanol, and isopropanol successively for 5 min each to remove organic matter, and then washed with deionized (DI) water (resistivity > 18.2 MΩ·cm, Barnstead Ultrapure Water System, Dubuque, IA) and dried with high purity nitrogen gas. The clean biotite flakes were stored in dust-free tubes for further batch experiments. Three phosphonates with different numbers of phosphonate functional groups, namely iminodi(methylene)phosphonate (IDMP), nitrilotris(methylene)phosphonate (NTMP), and diethylenetriaminepenta(methylene)phosphonate (DTPMP), were obtained from Sigma-Aldrich (Technical grade, St. Louis) and used as received (Table 6.1).

6.2.2 Batch Experiments

All batch experiments were conducted in a benchtop reactor (Parr Instrument Co., IL, Figure 2.1), simulating conditions relevant to engineered subsurface operations where CO₂ is injected for enhanced oil/gas production or geologic CO₂ sequestration (95 °C and 102 atm CO₂). Phosphonate solutions with a concentration of 0.5 mM were prepared in 0.5 M NaCl, mimicking the high salinity of subsurface brine and controlling the ionic strength. The initial pH of the solutions was adjusted to be 5.6 under ambient conditions, which resulted in an initial pH of around 3.2 under 95 °C and 102 atm CO₂, measured by
a high temperature and high pressure pH probe (4-S1 and Table 6.2). This in situ pH was close to that of control experiments without adding any phosphonate. The preparation process was open to air, leading to an initial dissolved oxygen concentration of around 8.9 mg/L. Biotite flakes were placed in PTFE tubes containing 4 mL of the prepared solutions, and the tubes were sealed in the reactor without access to light. Triplicate samples for each batch were prepared, and duplicate batch experiments were conducted. After reaction for a desired elapsed time (3, 8, 22, 44, and 70 h), the experiments were stopped, and the reactor was slowly degassed and cooled within 30 min. The degassing process was the same for all experiments. Thus, the differences among experiments resulted solely from the reactions.

Table 6.1 Abbreviations, chemical formulas, and structures of phosphonates used in this study.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Chemical Formula</th>
<th>Structure</th>
<th>Number of Functional Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>IDMP</td>
<td>C$_2$H$_9$NO$_6$P$_2$</td>
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<td>2</td>
</tr>
<tr>
<td>NTMP</td>
<td>C$<em>3$H$</em>{12}$NO$_9$P$_3$</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>3</td>
</tr>
<tr>
<td>DTPMP</td>
<td>C$<em>9$H$</em>{28}$N$<em>3$O$</em>{15}$P$_5$</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>5</td>
</tr>
</tbody>
</table>
6.2.3 Analysis of Aqueous Solutions

Aqueous complexation was analyzed with ultraviolet-visible spectroscopy (UV-Vis, Thermo Scientific Evolution 60S) by scanning the wavelength range of 200–500 nm for the reaction solutions after filtering them through 0.2 µm polypropylene membranes. Then the solutions were acidified in 1% trace metal nitric acid (HNO₃). The acidified solutions were measured for aqueous cation concentrations and total phosphorus by inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 7300 DV). To analyze the concentrations of phosphate and formate, two degradation products of phosphonates, ion chromatography (IC, Thermo Scientific Dionex ICS-1600) was used.

6.2.4 Characterization of Reacted Biotite Samples

The reacted biotite flakes were rinsed with DI water right after they were taken from the reactor, and then dried with high purity nitrogen gas. Next, their surface morphologies were measured using atomic force microscopy (AFM, Nanoscope V Multimode SPS, Veeco). Areas of 50 µm × 50 µm on the sample surfaces were scanned in contact mode with a nonconductive silicon nitride probe (tip radius of 10 nm, DNP-S10,
Bruker) at a rate of 0.999 Hz and a deflection point of 1.975 V. The AFM images were then analyzed with Nanoscope software (v7.20) and representative height mode images were reported. Scanning electron microscopy (SEM, Nova NanoSEM 230) was also used to characterize the reacted biotite basal surfaces. An electron accelerating voltage of 10.00 kV was used for imaging. The elemental composition of reacted biotite was measured by energy dispersive X-ray spectroscopy (EDX).

6.2.5 Identification of Secondary Mineral Phases

To identify the phases of secondary minerals formed on biotite surfaces and in solutions, high-resolution transmission electron microscopy (HR-TEM, JEOL-2100F) was used. The reacted biotite flake was sonicated in ethanol for 5 min to detach particles from the surface into the ethanol. Then a droplet of the suspension was placed on a Formvar/carbon coated-Cu grid (Electron Microscopy Science, PA) for imaging surface precipitates. To image particles formed in solution, a droplet of the reacted solution before filtration was placed on a TEM grid after centrifugation in DI water for five times, each time for 5 min at 5000 rpm. To prevent unexpected precipitation during sample drying, the centrifugation was performed to remove dissolved ionic species. EDX provided information about elemental compositions. Electron diffraction patterns and lattice fringes were obtained to identify the secondary mineral phases. In addition, the polypropylene membranes used for filtering the solutions were washed with DI water, dried, and examined by SEM for detached biotite layers and particles formed in the solutions.
6.2.6 Measurement of Water Contact Angles on Biotite Samples

The reacted biotite flakes were measured for contact angles by a contact angle analyzer (Surface Electro Optics, Phoenix 300) under ambient conditions. A biotite sample was placed in the sample stage, and then a droplet of DI water was deposited on the basal surface by a syringe needle. The droplet on the mineral surface was imaged and its contact angle was measured (Figure 4.1A). The measurement was repeated at least six times per experimental condition to obtain the average contact angle.

6.3 Results and Discussion

6.3.1 Degradation of Phosphonates

The chemical stabilities of the three phosphonates in the presence of biotite under the high temperature and high pressure conditions were different. Significant degradation of NTMP and DTPMP was observed, as shown by the evolution of phosphate and formate concentrations in Figure 6.1. In a recent study, we reported that reactive oxygen species (ROS) generated by the interaction between Fe(II) sites in biotite and dissolved molecular oxygen could degrade DTPMP (Chapter 7). Therefore, the degradation of NTMP and DTPMP here could also result from reaction with reactive oxygen species formed through oxygenation of biotite flakes. However, changes in phosphate and formate concentrations were not detected in the IDMP reaction system, indicating that IDMP was stable and its degradation was not significant over the course of the reaction. This observation was consistent with a report that, under ambient conditions, NTMP could be degraded to form IDMP with one phosphate released, while the further abiotic degradation of IDMP was considerably slower, due to the difference in structure.217 Specifically, the degradation of
phosphonates was reported to start with one-electron abstraction from N. The nitrogen (N) in NTMP and DTPMP connects to three -CH₂- groups, while the N in IDMP connects two -CH₂- groups and one -H, thus it would be more difficult to abstract one electron from the N in IDMP to initiate its degradation. The concentrations of phosphate and formate normalized by the number of phosphonate functional groups in NTMP (3) and DTPMP (5) were similar, suggesting their similar initial susceptibilities to be degraded by ROS. In addition, in both the NTMP and DTPMP systems, the concentrations of phosphate and formate increased quickly within 22 h reaction, and then slowed. Two mechanisms can explain the evolution of phosphonate degradation: First, the release of phosphate and formate by phosphonate degradation forms new phosphonates with fewer functional groups. The newly formed phosphonates (e.g., IDMP formed from NTMP) can be more stable than the original NTMP and DTPMP, leading to slower subsequent degradation. Second, the slower phosphonate degradation after reaction times longer than 22 h could result from the lower oxygen level in the reactor, because the reaction consumed oxygen and the reactor was sealed and isolated from air. It is also possible that the produced phosphate could be involved in secondary precipitation with cations released from biotite dissolution, thus inhibiting any further increase of its aqueous concentration. However, the increase of formate concentration was also limited after reaction times longer than 22 h, while formate was not supposed to form significant precipitation. For this reason, we conclude that secondary mineral precipitation is not a main mechanism.
Figure 6.1 Concentrations of phosphate and formate from NTMP and DTPMP degradation with biotite, normalized by their numbers of functional groups, at 95 °C and 102 atm CO₂. Error bars are the standard deviations of triplicate samples in duplicate experiments. IDMP degradation was not detected.

6.3.2 Phosphonates Promoted Biotite Dissolution

The presence of phosphonates affected the evolution of aqueous cation concentrations, but without big differences among phosphonates, as shown by the ICP-OES results in Figure 6.2. Regarding interlayer K, phosphonates did not affect its aqueous concentrations compared to those observed for the control system. This result occurred because of similar extents of ion-exchange reactions in the systems, where the initial pH and ionic strength of the reaction solutions were adjusted to be same.\(^\text{79, 187}\) For Si and Mg, higher concentrations were observed for all the three phosphonate systems than for the control, suggesting that phosphonates promoted biotite dissolution. However, the aqueous concentrations of Al and Fe in phosphonate systems were generally lower than those in the control system. The solubility constants \(K_{sp}\) of Fe- and Al-bearing
phosphonate/phosphate minerals are on the order of $10^{-19}$ or lower, suggesting that they are quite insoluble.\textsuperscript{189, 198-199} We have also recently reported that the presence of phosphate and DTPMP promoted precipitation of secondary Fe- and Al-bearing minerals.\textsuperscript{187} Note that the ICP-OES measured the net concentrations of cations from biotite dissolution and secondary mineral precipitation. Thus, we hypothesized that IDMP and NTMP or released phosphate from NTMP degradation promoted precipitation of secondary Fe- and Al-bearing minerals, as in the DTPMP system, thereby leading to the lower aqueous Al and Fe concentrations.

To investigate the mechanisms underlying the indistinguishable net Si and Mg concentrations and the slightly different Al and Fe concentrations, we then considered phosphonate structure-dependent aqueous complexation and surface complexation affecting mineral dissolution and secondary mineral precipitation.

\textbf{Figure 6.2} Aqueous concentrations of K, Si, Al, Mg, and Fe from biotite dissolution experiments with 0.5 mM of different phosphonates, at 95 °C and 102 atm CO\textsubscript{2}. Error bars are the standard deviations of triplicate samples in duplicate experiments.
Aqueous complexation was identified by the UV-Vis spectra of the reacted solutions (Figure 6-S1). In both the NTMP and DTPMP reaction solutions, a peak in 250–260 nm was observed, which indicated Fe(III)-phosphonate aqueous complexes. Aqueous complexation between cations and organic ligands could reduce the activity of cations and increase the apparent solubility of minerals. Our study in Chapter 5 found that the aqueous complexation of Fe(III)-DTPMP contributed to promoting biotite dissolution. By the same mechanism, aqueous complexation of Fe(III)-NTMP could also promote biotite dissolution. However, in the IDMP system, the peak did not show up clearly, indicating that aqueous complexation was not significant. Figure 6.3 shows the absorbance of Fe(III)-phosphonate aqueous complexes at 260 nm in the three phosphonate systems over time. Consistent with the literature, DTPMP containing five phosphonate functional groups had the largest extent of aqueous complexation with Fe(III), then NTMP, and IDMP. Thus, DTPMP was expected to promote the most biotite dissolution, although this was not the case on the basis of the evolution of measured aqueous cation concentrations (Figure 6.2). Hence, in addition to aqueous complexation, other mechanisms, such as surface complexation and secondary mineral precipitation, should also be considered and are discussed in later sections.
Figure 6.3 Evolution of aqueous complexation over time in phosphonate systems after reactions with biotite at 95 °C and 102 atm of CO₂.

6.3.3 Structure-dependent Effects of Phosphonates on Biotite Surface Morphology Alteration and Secondary Mineral Precipitation

In addition to the aqueous phase, phosphonates significantly altered the morphology of the basal surfaces of biotite. The alterations were dependent on phosphonate structures, as shown by the AFM images in Figure 6.4 and SEM images in Figure 6.5. Compared with the control sample, the presence of IDMP significantly promoted secondary mineral precipitation on biotite basal surfaces, even at the early reaction times of 3 h and 8 h (Figure 6.4). However, within 8 h reaction, the formation of surface precipitation was less extensive on the NTMP and DTPMP samples than that on the IDMP samples. In the presence of IDMP, the SEM image of a 3 h biotite sample (Figure 6.5) shows spherical particles in addition to fibrous illite precipitates. EDX analyses of the reacted biotite surfaces indicated that, after 3 h reaction, the main elemental composition
Figure 6.4 Height mode AFM images of biotite basal surfaces after reaction at 95 °C and 102 atm CO₂. The AFM images are 50 µm × 50 µm. To highlight differences, the height scale is 200 nm for the images with blue diamonds and 60 nm for the other images.

of biotite remained, while there was a higher phosphorus (P) amount on the IDMP sample surface (Figure 6-S2). Considering that IDMP contains the fewest phosphonate functional groups, the EDX observations suggest that, compared to the other phosphonates, there was higher extent of surface IDMP complexation and adsorption, and consequently more significant surface precipitation. The greater surface adsorption by IDMP than NTMP and DTPMP was consistent with reports that phosphonate adsorption decreases with increasing phosphonate functional groups. IDMP surface adsorption might promote both
biotite dissolution and subsequent secondary mineral precipitation on mineral surfaces. After 22 h reaction, many precipitates formed on the NTMP and DTPMP samples. The difference in induction times of the surface precipitation in different phosphonate systems might result from different extents of available aqueous complexation and surface complexation. The strongest aqueous complexation in the DTPMP system, indicated by UV-Vis absorption data (Figure 6.3), increased mineral apparent solubility and slowed the surface precipitation. SEM images of 22 h and 44 h phosphonate samples (Figure 6.5) show cracked biotite layers, bending outwards and detaching from biotite basal surfaces. Consistent with a recent report, the bent layers were probably due to adsorption of large phosphonate molecules (Chapter 5).

![SEM images of reacted biotite basal surfaces. The yellow arrows indicate the bent surface cracked layers.](image)

**Figure 6.5** SEM images of reacted biotite basal surfaces. The yellow arrows indicate the bent surface cracked layers.
To identify the phases of surface precipitates, particles formed on biotite were detached and measured with TEM (Figure 6.6A). Lattice fringe information indicated that the particles formed on biotite surface after reaction with IDMP were P, Fe, and Al-rich amorphous phases, while the surface particles in NTMP and DTPMP samples were crystallized. The d-spacing of 2.73 Å in surface particles in the NTMP sample highly suggested the presence of an P, Fe, and Al-bearing phosphate mineral, vauxite (FeAl₂(PO₄)₂(OH)₂). In the DTPMP system, the surface particles were found to be a mixture of gibbsite (Al(OH)₃), strengite (FePO₄), and berlinite (AlPO₄) (Chapter 5). The differences in the secondary mineral phases were probably due to the absence or presence of phosphate: NTMP and DTPMP degraded to release phosphate, while IDMP did not.

Figure 6.6 TEM measurements of particles formed (A) on biotite surfaces and (B) in solutions after 70 h reaction at 95 °C and 102 atm CO₂.
Detached biotite layers and homogeneously precipitated amorphous Fe- and Al-bearing minerals in solution were reported in the 0.5 mM DTPMP system in Chapter 5. In the present work, particles in the reacted solutions with IDMP and NTMP were also collected and measured by SEM (Figure 6.7). After 44 h reaction, in the IDMP system (Figure 6.7A2), abundant microscale platy particles and aggregates of needle-like particles were observed, and both mainly contained P, Fe, and Al (Figure 6-S3). In the NTMP and DTPMP systems (Figure 6.7A3 and A4), we did not observe the aggregates of needle-like particles. After 70 h reaction, in the NTMP system (Figure 6.7B3), in addition to the platy-like microscale particles and tiny spherical particles, aggregates of needle-like particles were formed. This was probably due to the accumulation of IDMP resulting from NTMP degradation. Therefore, the morphology of secondary precipitates also depends on the structure of phosphonates. Compared with the IDMP and NTMP systems, the amount of homogeneous secondary precipitates was much higher in the DTPMP system (Figure 6.7). There were also tiny spherical particles, which were not resolved clearly by SEM (Figure 6.7). Further, to identify the tiny spherical particles, TEM was utilized. Similar to those in the DTPMP system, the results indicated that the particles in the IDMP and NTMP systems were amorphous phases (Figure 6.6B), with abundant P, Fe, and Al (Figure 6-S4).

Taken together, phosphonates affected both biotite dissolution and precipitation, with similar net effects, as indicated by the evolution of aqueous cation concentrations. However, the mechanisms underlying the effects of phosphonates were dependent on phosphonate structures. In the presence of phosphonates, precipitation of P, Fe, and Al-bearing minerals was enhanced, leading to lower aqueous Fe and Al concentrations than in the control experiments. Phosphonates containing more phosphonate functional groups had
larger extents of aqueous complexation, promoting biotite dissolution and later heterogeneous surface precipitation. On the other hand, IDMP, containing the fewest functional groups, had great surface complexation, promoting both biotite dissolution and faster surface precipitation. There was more significant homogeneous precipitation in the DTPMP system than in the IDMP and NTMP systems. The IDMP structure is key in controlling the formation of needle-like aggregated particles and phosphate released from phosphonate degradation is key in controlling the crystallinity of surface precipitates. As a result of degradation, NTMP decomposed to form IDMP and behaved like IDMP. Due to limitations of both the current experimental results and the literature on phosphonate surface complexation, it remains unclear how configurations of phosphonate surface complexation and molecular pathways specially control the morphologies and phases of secondary precipitates.

![Figure 6.7](image)

**Figure 6.7** SEM measurements of samples collected on membranes used for filtering solutions after (A) 44 h and (B) 70 h reactions. The images in the third row were taken from the corresponding samples, indicated by the same color borders. The blue arrows indicate detached biotite layers, orange arrows indicate needle-like aggregates, yellow arrows indicate platy particles, and green arrows indicate tiny spherical particles (aggregates). The EDX analyses of these particles are shown in Figure 6-S3.
6.3.4 Enhanced Surface Wettability by Phosphonate Adsorption

Phosphonate–biotite interactions significantly impacted biotite wettability, which is an important mineral property affecting the flow of reactive fluids during subsurface operations. This change is evident in the alterations of contact angles shown in Figure 6.8. The contact angles of control samples without any phosphonates were around 28°. However, for biotite samples after reaction with phosphonates, much lower contact angles (around 11°) were observed, showing that phosphonate–biotite reactions enhanced biotite surface wettability. Surface roughness enhances wettability by supporting and stabilizing thicker water films on hydrophilic surfaces. In AFM images (Figure 6.4), the surface roughness of the reacted biotite samples differed for different phosphonates, particularly after 3 h and 8 h of reaction. In other words, the surface roughness increased with time, in particular for the NTMP and DTPMP samples. However, the contact angles for phosphonate samples did not change over time, which was consistent with report in Chapter 5 for DTPMP samples. Therefore, surface roughness was not the main contributor to the lower contact angles observed for phosphonate samples. It has been observed in Chapters 4 and 5 that adsorption of phosphate and DTPMP significantly enhances biotite surface wettability by exposing hydrophilic groups, with a stronger effect by DTPMP adsorption. However, IDMP was stable and no phosphate from IDMP degradation was detected during the course of reaction. Hence, the enhanced wettability of biotite samples in the IDMP system was attributed mainly to the adsorption of IDMP on biotite. The number of phosphonate functional groups in NTMP is in between those of IDMP and DTPMP, so we can assume that NTMP adsorption also played a dominant role in enhancing the wettability of biotite. The time-independent contact angles observed for
phosphonate samples indicated that a small amount adsorption of phosphonates exposed enough amount of hydrophilic functional groups to enhance the surface wettability, and more adsorption after a longer reaction time did not further change the contact angles.

![Graph showing contact angle vs reaction time for different phosphonates.](image)

**Figure 6.8** Wettability analyses of biotite basal surfaces after reaction with different phosphonates over time at 95 °C and 102 atm CO$_2$. The error bars are standard deviations of six measurements from triplicate samples in duplicate experiments.

In addition, the effects of phosphonate adsorption on wettability alteration were not dependent on the structure of the phosphonates. The structure-independent enhancement effects by the three phosphonates were consistent with the time-independent effects of phosphonates that adsorption of even a small amount of phosphonate sufficed to make biotite surfaces more hydrophilic. Moreover, although we observed a slightly higher amount of P on biotite surfaces after reaction with IDMP for 3 h (**Figure 6-S2**), similar amounts of phosphonate functional groups might be exposed on biotite surfaces among the three phosphonates after longer reaction times. The changes in total P concentrations after 70 h (**Figure 6-S5**) were about 80%, 50%, and 30% respectively for IDMP, NTMP, and DTPMP, all corresponding to an approximate 0.8 mM loss of phosphonate functional
groups, due to both adsorption and precipitation. Based on the evolution of aqueous cation concentrations, we roughly assumed that the total amounts of secondary precipitates in the three phosphonate systems were very similar. Therefore, the numbers of phosphonate functional groups exposed on biotite surfaces after phosphonate adsorption could also be similar, resulting in similar extents on wettability alteration.

6.4 Environmental Implications

This study presented experimental evidence on the chemical stability of phosphonates and structure-dependent effects of phosphonates in brine–biotite interactions and discussed their dominant mechanisms. IDMP was stable under subsurface relevant conditions, while NTMP and DTPMP degraded, forming new phosphonates and releasing phosphate and formate. The degradation of phosphonates reduces their aqueous concentrations and alters their structures, which may affect their performance in scale inhibition. Furthermore, phosphonates promoted biotite dissolution and enhanced secondary precipitation of P, Fe, and Al-bearing minerals. With increasing numbers of phosphonate functional groups in phosphonate structures, their effects change from surface complexation-dominant to aqueous complexation-dominant. Phosphonates with different structures also affected the morphologies, phases, and distributions of secondary precipitates, which can further influence the porosity and permeability of reservoir rocks to different extents.

The wettability of biotite was found to be enhanced by phosphonates, however, their effects were structure-independent. Adsorption of a small amount of phosphonates on biotite surfaces exposed enough hydrophilic hydroxyl groups to enhance wettability. The
altered wettability will impact the transport of related reactive fluids in subsurface sites. The information provided here can be useful to evaluate future phosphonate applications by systematically considering their chemical stability, chelating capability, and effects on mineral dissolution and secondary mineral precipitation.

Acknowledgments

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Supporting Information for Chapter 6

6-S1. UV-Vis analyses

![UV-Vis Spectra](image)

**Figure 6-S1** UV-Vis spectra of the reacted phosphonate solutions.

6-S4. SEM and TEM measurements

![SEM-EDX Analyses](image)

**Figure 6-S2** SEM-EDX analyses of biotite basal surfaces after 3 h reaction. The yellow boxes indicate the EDX measurement locations.
**Figure 6-S3** SEM-EDX results for particles formed (Figure 6) in the IDMP and NTMP systems after 40 h and 70 h reaction under 95 °C and 102 atm CO$_2$. M/Al indicates the atomic ratio of M (Fe, Mg, Si, P, and Al) to Al.

**Figure 6-S4** TEM-EDX results for small spherical particles formed in reaction solutions after 70 h under 95 °C and 102 atm CO$_2$. M/Al indicates the atomic ratio of M (Fe, Mg, Si, P, and Al) to Al.
6-S5. Evolution of total aqueous P concentrations

Figure 6-S5 Evolution of total aqueous P concentrations with time after reaction under 95 °C and 102 atm CO$_2$. 
Chapter 7. Redox Degradation of DTPMP with Fe-bearing Phyllosilicates under High Temperature and Pressure Conditions

Abstract

In Chapters 5 and 6, we elucidated the effects of phosphonate concentrations and phosphonate structures on the chemical reactions of biotite. During the experimental investigation, we learned that phosphonates were degraded in the presence of biotite. To further address this finding, in this chapter, we reacted 0.5 mM DTPMP (diethylenetriaminepenta(methylene)phosphonate, a model phosphonate) under subsurface relevant conditions (i.e., slightly oxic, 50–95 °C and 102 atm CO₂), we reacted 0.5 mM DTPMP (diethylenetriaminepenta(methylene)phosphonate, a model phosphonate) with three phyllosilicates: an Fe-poor muscovite, an Fe(II)-rich biotite, and an Fe(III)-rich nontronite. The three phyllosilicates induced different effects on DTPMP degradation, with no distinguishable effect by muscovite, slight promotion by nontronite, and remarkable promotion by biotite. We found that Fe associated with phyllosilicates is key to the redox degradation of DTPMP: reactive oxygen species (ROS) were generated through the reduction of molecular oxygen by Fe(II) adsorbed on mineral surface or in mineral structure, and the hydroxyl radicals further degraded DTPMP to form phosphate, formate, and DTPMP residuals. In addition, DTPMP degradation was favored at higher
temperatures, probably due to more exposed reactive Fe(II) sites created by enhanced biotite dissolution and also due to faster electron transfers. Dissolved Fe and Al precipitated with phosphate or degraded DTPMP and formed secondary minerals. This study provides new information about how DTPMP degradation is affected by the reactivity of Fe-bearing phyllosilicates and has implications for engineered subsurface operations.

7.1 Introduction

Led by new applications of horizontal drilling and hydraulic fracturing, CO$_2$-enhanced unconventional oil and gas recovery from shale reservoirs has been rapidly growing.$^{2-4}$ Pressurized fracking fluids are pumped into the wellbores to crack the rocks to increase permeability and release natural gas, petroleum, and brine, and allow them to flow more freely.$^{220}$ To prevent the formation of mineral scales in the wellbores and cracked rocks, which can reduce their porosity and permeability, chemical scale inhibitors are added to the fracking fluids. After scale inhibitors are injected, at a concentration above the minimum inhibitor concentration, they inhibit scale formation by affecting the processes of nucleation or crystal growth of scale minerals.$^{166, 192, 194}$ To maintain an effective concentration of scale inhibitors and ensure their efficacy, it is important to understand their fate and transport under subsurface environments.

Phosphonate chelating agents are widely used as scale inhibitors during hydraulic fracturing.$^{192, 208}$ The average concentrations of scale inhibitors in fracking fluids are reported to be around 0.023% by weight percent ($\sim$0.5 mM).$^{33}$ Phosphonate scale inhibitors contain more than one phosphonate functional group (-PO$_3$H$_2$), and C-P and/or C-N bonds. Normally, phosphonates are stable towards chemical hydrolysis and thermal
decomposition. However, photodegradation of phosphonates was reported when they complexed with Fe(III), while under non-illuminated conditions no degradation of phosphonates occurred. It is well known that reactive oxygen species (ROS) generated from photolysis are a predominant factor in controlling the fate of redox-active substances. In addition, under non-illuminated conditions, it has also been reported that ROS generated from systems containing Cu$^{2+}$/H$_2$O$_2$, Fe$^{2+}$/H$_2$O$_2$, and Mn(II)/O$_2$ could facilitate the degradation of phosphonates. In this process, phosphate and formate were reported as the two main degradation products of phosphonates. Based on all the previous studies, the stability of phosphonates greatly depends on the generation of ROS, which is affected by factors such as light condition, metal ions, and oxygen. Hence, to better understand the stability of phosphonates during engineered subsurface operations, a systematic investigation of phosphonate degradation is needed under conditions relevant to subsurface sites.

Subsurface environments are usually dark. The temperature and pressure are high in subsurface sites for energy-related operations, falling in the ranges of 31–110 °C and 73.6–600 atm, respectively. Shales, which contains abundant phyllosilicates, are the main subsurface reservoirs for unconventional oil and gas recovery. Iron(II/III)-bearing phyllosilicate minerals, with different iron contents and iron oxidation states, are ubiquitous in subsurface systems. The dissolution and secondary precipitation of phyllosilicate minerals can affect the hydrogeological properties of reservoirs, thus affecting the subsurface operations. Furthermore, the Fe sites in phyllosilicates have been reported to play a critical role in various redox processes, e.g., reduction of chromium(VI) and nitrate, and oxidation of arsenic (III). Although
subsurface sites are often under reducing conditions with deficient oxygen, molecular oxygen can be introduced into subsurface environments through natural or artificial processes, such as surface water and groundwater interactions or injection of fracking fluids,\textsuperscript{231-233} altering the subsurface redox conditions. However, under these conditions, the effects of phyllosilicates on the generation of ROS, and consequently on the stability of phosphonates, are unclear.

Therefore, the objective of this study was to investigate the impacts of Fe-bearing phyllosilicates on the degradation of phosphonates, employing commonly used DTPMP scale inhibitor as a model, under conditions relevant to subsurface environments. We further elucidated the reaction mechanisms. We report here that DTPMP degradation was promoted in the presence of Fe(II)-bearing phyllosilicates through the generation of reactive oxygen species from reduction of molecular oxygen. Degradation of DTPMP reduced the available aqueous DTPMP concentration, which may affect its scale inhibition performance. In addition, significant secondary precipitates were formed. The DTPMP degradation, mineral dissolution and secondary precipitation may further impact reservoir porosity and permeability. This study provides new findings about the effects of Fe-bearing phyllosilicates on DTPMP degradation under high temperature and high pressure conditions, results having important implications for understanding the fate and transport
of chemical additives during engineered subsurface operations and benefiting their sustainable design.

7.2 Experimental Section

7.2.1 Chemicals and Minerals

Technical-grade diethylenetriaminepenta(methylene)phosphate (DTPMP, \( \text{C}_{9}\text{H}_{28}\text{N}_{3}\text{O}_{15}\text{P}_{5} \)) was obtained from Sigma-Aldrich. The active concentration of DTPMP in the purchased chemical is 50% by weight, and there is 15% HCl (hydrochloric acid) and 35% H\(_2\)O (water). To control the ionic strength and mimic the high salinity in subsurface sites,\(^{26}\) reaction solutions of 0.5 mM DTPMP were prepared in 0.5 M NaCl.

Biotite and muscovite purchased from Ward’s Natural Science, and nontronite (NAu-1) purchased from the Source Clays Repository of the Clay Minerals Society, were used to examine the effects of Fe in mineral structure on DTPMP degradation. They are all phyllosilicates, having 2:1 layer structures composed of two opposing tetrahedral sheets and an octahedral sheet with an interlayer filled by cations to balance the charge. However, their Fe contents and Fe oxidation states are different and were characterized as described later. To remove organic matter, the minerals were sonicated in acetone, ethanol, and isopropanol respectively for 5 min, washed with deionized (DI) water (resistivity > 18.2 M\(\Omega\)-cm, Barnstead Ultrapure Water Systems), and dried with high purity nitrogen gas. Then they were ground with stainless grinders, and particles between 53–106 \(\mu\)m were isolated by sieves for use in further experiments. The specific surface areas measured by the Brunauer-Emmett-Teller (BET) method were 2.99 m\(^2\)/g, 2.49 m\(^2\)/g, and 75.1 m\(^2\)/g for biotite, muscovite, and nontronite, respectively. The chemical composition of the biotite
was analyzed with X-ray fluorescence (XRF) and found to be $K_{0.91}Na_{0.08}Ca_{0.05}Mg_{1.72}Mn_{0.06}Fe_{1.12}Ti_{0.12}Al_{1.00}Si_{2.98}O_{10}(F_{0.51}(OH)_{0.49})_2$ (Table 2.1). The empirical chemical formula for muscovite is $KAl_2(AlSi_3O_{10})(F,OH)_2$; for nontronite it is $Na_{0.3}Fe_2(AlSi_3O_{10})(OH)_2$. The contents of Al, Si, and Fe in muscovite and nontronite were measured with scanning electron microscopy with energy-dispersive X-ray microscopy (SEM-EDX, Nova NanoSEM 230) and are shown in Table 7.1.

Table 7.1 Contents of Al, Si, and Fe in muscovite and nontronite used in this study, analyzed with SEM-EDX (unit: wt%).

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscovite</td>
<td>19.7</td>
<td>23.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Nontronite</td>
<td>5.2</td>
<td>21.2</td>
<td>28.4</td>
</tr>
</tbody>
</table>

A modified digestion-ferrozine method was used to characterize the extents of Fe(II) and Fe(III) in the phyllosilicates used in this study. A mass of 0.2 g minerals was digested in 30 mL of 9 M HCl for 2 h. The sample was then filtered, and the filtrate was diluted to 40 mL. Taking 0.1 mL of the diluted solution to 4.9 mL of ferrozine solution, we performed ultraviolet-visible spectroscopy (UV-Vis, Thermo Scientific Evolution 60S) to measure the absorbance at 562 nm, which indicated Fe(II). The ferrozine solution was prepared by adding 1 g of ferrozine (Sigma-Aldrich) to 1 L of 50 mM HEPES buffer (pH 7). Fe(II) standards were prepared with ferrous ethylenediammonium sulfate (Sigma-Aldrich), and a calibration curve relating absorbance and Fe(II) concentration was obtained. Another 10 mL of the diluted solution was mixed with 1 mL hydroxylamine (NH$_2$OH) (100 g/L), which reduced Fe(III) to Fe(II), and was boiled for 10 min. After the solution cooled, the Fe(II) was again quantified by the UV-Vis method as described above, which indicated
the total Fe content. The caveat of this measurement process for muscovite can be found in 7-S1 in the Supporting Information for Chapter 7.

**7.2.2 DTPMP Degradation Experiments**

DTPMP degradation experiments were conducted in a high temperature and high pressure reactor (Parr Instrument Co., IL, Figure 7.1). The experimental setup allowed *in situ* sampling after reaction for elapsed times of 1, 3, 5, 10, and 22 h. In a 300 mL Teflon cup, prepared phyllosilicate powders (0.0375 g) were mixed with 150 mL of 0.5 mM DTPMP solution, with a solid to liquid ratio of 0.25 g/L. The mixtures were prepared in an open system, allowing air to dissolve. The measured dissolved oxygen concentration was around 8.9 mg/L. Next, the Teflon cup was sealed in a stainless reactor. In this way, the reaction mixture did not have access to light and photodegradation was halted. The reaction suspensions were stirred during the experiments to obtain a well-mixed system. To examine the effects of temperature, the temperature conditions for the DTPMP degradation with biotite experiments were 50 °C, 70 °C, and 95 °C. The pressure was set at 102 atm CO$_2$ to simulate the high pressure in subsurface operations. The dissolved oxygen concentration after the injection of CO$_2$, measured *ex situ*, was around 2.4 mg/L, probably due to oxygen consumption and oxygen replacement by CO$_2$. The initial pH of the solutions was adjusted to pH 5.6 prior to experiments, which resulted in an initial *in situ* pH of around 3.2 under the high temperature and high CO$_2$ pressure experimental conditions. The initial pH was within the pH ranges in subsurface sites for engineered operations. Control experiments were performed without adding any minerals.
To prepare reacted biotite samples for better characterization of surface morphology alteration, DTPMP degradation experiments were also conducted with clean 1.0 cm × 0.8 cm biotite flakes with a thickness of 80 ±10 μm at 50 °C, 70 °C, and 95 °C, all under 102 atm of CO₂.

### 7.2.3 Characterization of Aqueous Solutions and Minerals

Aqueous samples were filtered along the reaction course. The concentrations of phosphate and formate, two of the degradation products,$^{205}$ over time were monitored by ion chromatography (IC, Thermo Scientific Dionex ICS-1600). The concentrations of aqueous cations released from mineral dissolution were measured with inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 7300 DV).

After 22 h reaction, the reactor was allowed to cool and degas over 30 min. Previous studies have reported that the degassing process did not change the aqueous solutions and secondary minerals.$^{79, 187}$ The solutions were centrifuged at 5000 rpm for 5 min. The supernatant, containing dissolved ionic species, was discarded, then 40 mL of DI water
was added, and the suspension was centrifuged again. The process was repeated for 10 times to remove ionic species and wash the mineral powders to prevent secondary mineral precipitation after reactions. The minerals were collected, oven-dried overnight, and analyzed with SEM. A 10.00 kV electron accelerating voltage was used for the measurements. The elemental compositions of the minerals were analyzed with EDX during the SEM measurements. The particles observed to be not attached to biotite surfaces were assumed to be homogeneous precipitates (mainly formed in the solution), and those on biotite surfaces were assumed to be heterogeneous precipitates. The reacted biotite flakes were also characterized with SEM to assess the surface morphology changes. The phyllosilicate minerals before reaction were measured for comparison (Figure 7-S1).

7.2.4 Examination of Reactive Oxygen Species

Tert-butyl alcohol (TBA) was used to scavenge hydroxyl radicals during DTPMP degradation. The boiling point of TBA is around 82 °C under ambient conditions. To retain TBA in the reaction solutions, DTPMP degradation experiments with TBA were conducted at 70 °C and 102 atm of CO₂. The concentration of the TBA scavenger added was 50 mM. After desired reaction times, aqueous samples were taken for measurements of phosphate and formate concentrations.

To check if superoxide (O₂⁻) was formed during the reaction, nitro blue tetrazolium (NBT) with a concentration of 0.1 mM and TBA with a concentration of 50 mM were added together into the biotite reaction suspension (0.25 g/L) at 70 °C and 102 atm CO₂. After 22 h reaction, the suspension was scanned from 400 to 800 nm by a UV-Vis spectrometer. To check hydrogen peroxide (H₂O₂), biotite powders were first reacted in 0.5 mM DTPMP solution with a solid to liquid ratio of 0.25 g/L at 95 °C under ambient
pressure. Then a photometric method was used to determine the presence of $\text{H}_2\text{O}_2$. After 22 h reaction, 27 mL of filtered reaction solution was mixed with 3 mL of buffer solution, prepared by mixing 0.5 M Na$_2$HPO$_4$ and 0.5 M NaH$_2$PO$_4$, to achieve pH 6. Next, 50 µL of DPD (N,N-diethyl-1,4-phenylenediammonium sulfate) reagent solution and 50 µL of POD (peroxidase) reagent were added. The DPD reagent was prepared by adding 0.1 g of DPD to 10 mL 0.1 M H$_2$SO$_4$, and the POD reagent was prepared by dissolving 10 mg of POD in 10 mL DI water. The absorption spectrum of the mixed solution was scanned from 400 to 600 nm by a UV-Vis spectrometer.

### 7.3 Results and Discussion

#### 7.3.1 Effects of Phyllosilicates on DTPMP Degradation

The three phyllosilicates induced different extents of DTPMP degradation. The concentrations of phosphate and formate after DTPMP reaction with phyllosilicates at 95 °C are shown in Figure 7.2. In the control experiment without adding any minerals, the phosphate and formate concentrations did not change much with time, indicating DTPMP was stable during the experimental period. Compared with the control experiments, the effects of muscovite and nontronite on DTPMP degradation were not obvious, and similar or slightly higher aqueous concentrations of phosphate and formate were observed. However, in the biotite system, the evolutions of the aqueous concentrations of phosphate and formate were much faster than those in the control system, with increases of around 0.3 mM phosphate and 0.2 mM formate after 22 h reaction. This difference confirms that DTPMP degradation was significantly promoted by biotite. Note that even before the experiments, the concentrations of phosphate and formate were nonzero and were around...
0.4 mM and 0.04 mM in the prepared solutions, respectively. The initial phosphate and formate concentrations were probably impurities introduced during DTPMP production. However, because the same initial DTPMP concentrations, and thus the same initial phosphate and formate concentrations, were prepared for all the degradation experiments with different phyllosilicates, the comparison of the concentration evolutions of phosphate and formate are valid. In sum, the effects of the three phyllosilicates on DTPMP degradation varied: biotite significantly promoted the degradation of DTPMP, nontronite showed slight promotion, and muscovite barely affected DTPMP degradation.

Figure 7.2 Aqueous concentrations of phosphate and formate resulting from DTPMP degradation, at a salinity of 0.5 M NaCl and initial DTPMP concentration of 0.5 mM at T = 95 °C and P_{CO2} = 102 atm. Error bars are the standard deviation of triplicate experiments.

Table 7.2 Contents of Fe(II) and Fe(III) in phyllosilicates used in this study.

<table>
<thead>
<tr>
<th></th>
<th>Fe(II) (wt%)</th>
<th>Total Fe (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscovite</td>
<td>N/A</td>
<td>0.13</td>
</tr>
<tr>
<td>Biotite</td>
<td>14.04</td>
<td>14.63</td>
</tr>
<tr>
<td>Nontronite</td>
<td>0.23</td>
<td>21.35</td>
</tr>
</tbody>
</table>
Regarding the mechanisms of the different effects of phyllosilicates, we considered the roles of the contents and oxidation states of Fe sites in phyllosilicate structures in DTPMP degradation. The total Fe contents by weight percent in biotite, muscovite, and nontronite were characterized to be approximately 15%, 0.13%, and 21%, respectively (Table 7.2). The Fe in biotite structure was determined by the ferrozine method to be mainly Fe(II) (14%), while nontronite contained almost all Fe(III) in its structure. Although nontronite contains the highest amount of Fe, and the Fe is in its oxidized form, nontronite was much less effective in promoting DTPMP degradation than biotite. Moreover, during the high temperature and high pressure reactions, biotite dissolved and released Fe into the aqueous solutions (Figure 7.3). It was possible that aqueous Fe or Fe that adsorbed on mineral surfaces affected DTPMP degradation. Therefore, the effects of aqueous Fe(II) and adsorbed Fe(II) on muscovite on DTPMP degradation were also tested (Figure 7.2). To make the aqueous conditions comparable with the DTPMP-biotite reaction system and to have enough aqueous Fe(II) or adsorbed Fe(II), the concentration of Fe(II) added was about twice the highest aqueous Fe concentration in the DTPMP-biotite reaction system (i.e., 0.3 mM Fe(II)). The results showed that aqueous Fe(II) did not affect the degradation of DTPMP. The released phosphate might precipitate with Fe(II) added,¹⁸⁷ and so it was difficult to characterize the amount of Fe(II) adsorbed onto muscovite surfaces. However, it is clear that Fe(II) associated with muscovite promoted DTPMP degradation but was less effective than that in the biotite system. Therefore, we hypothesized that Fe(II) in biotite structure or associated with mineral structure was key to promoting DTPMP degradation. Previous studies have reported the role of phyllosilicates in the heterogeneous Fenton reaction and the production of ROS from oxygenation of phyllosilicates containing Fe(II),
such as reduced biotite and nontronite.\textsuperscript{231, 239} Hence, ROS generated by Fe(II) sites within biotite with oxygen can be involved in the degradation of DTPMP.

### 7.3.2 DTPMP Oxidation by Reactive Oxygen Species

No increases in phosphate and formate concentrations over time were observed with 0.05 M tert-butyl alcohol (TBA), as shown in Figure 7.4. The presence of TBA removed ·OH in the reaction systems and thus inhibited the degradation of DTPMP. This finding suggests that ·OH plays the dominant role in DTPMP degradation. This finding suggests that ·OH was generated through in the reaction system and played the dominant role in DTPMP degradation. Molecular oxygen can be reduced stepwise through one-electron transfer to form ROS, including superoxide (O$_2^-$), hydrogen peroxide (H$_2$O$_2$), and hydroxyl radical (·OH), with the first step of single electron transfer to molecular oxygen being thermodynamically unfavorable.\textsuperscript{180, 240} It has also been reported that catalysis by Fe(II) in pyrite, FeS$_2$, can allow two electrons to be added to molecular oxygen in one step, leading to the formation of H$_2$O$_2$ and avoiding the endergonic first step of forming O$_2^-$·\textsuperscript{241-242} To test the possible mechanisms, in the presence of both 0.1 mM NBT and 50 mM TBA, we observed the reduction of NBT by O$_2^-$ (Figure 7.5A), indicating the involvement of O$_2^-$ in the production of ·OH. Additionally, we observed the presence of H$_2$O$_2$ in the reaction suspension, indicated by the absorption peaks at around 510 nm and 550 nm from the UV-Vis spectra (Figure 7.5B).\textsuperscript{238} Therefore, in the biotite system, both O$_2^-$ and H$_2$O$_2$ were intermediates in the production of ·OH from reduction of O$_2$ by biotite. Recent studies reported that Fe(II), either as a structural component of silicate minerals or as adsorbed Fe(II), shifts the redox potential of the ferrous/ferric couple downward, making it a better electron donor.\textsuperscript{243-247} Consistent with the references, we found that aqueous Fe(II) did not
affect DTPMP degradation, further suggesting that Fe(II) associated or within phyllosilicate structures is more effective in transforming O$_2$ to ·OH.

**Figure 7.3** Dissolved concentrations of K, Si, Mg, Al, and Fe from biotite after reaction in 0.5 M DTPMP solution with a salinity of 0.5 M NaCl at different temperatures (50, 70, and 95 °C) and 102 atm of CO$_2$. Error bars are the standard deviation of triplicate experiments.

**Figure 7.4** Aqueous concentrations of phosphate and formate from DTPMP degradation at different temperatures (50, 70, and 95 °C) with a salinity of 0.5 M NaCl and initial DTPMP concentration of 0.5 mM at 102 atm of CO$_2$ in the presence of biotite. TBA was added as scavenger for hydroxyl radicals during DTPMP degradation at 70 °C. Error bars are the standard deviation of triplicate experiments.
A. Superoxide:

![Absorbance vs Wavelength](image)

B. Hydrogen peroxide:

![Absorbance vs Wavelength](image)

**Figure 7.5 (A).** UV-Vis absorption spectra obtained for suspensions before and after reaction with 0.1 mM NBT and 50 mM TBA. (B). UV-Vis absorption spectra of the filtered solution after 22 h reaction mixed with DPD and POD reagents.

Therefore, by one-electron transfer mechanism, molecular O₂ was reduced to form O₂⁻ and H₂O₂, and then -OH through catalysis by Fe(II) associated with minerals (biotite structural Fe(II), adsorbed Fe(II), or neoformed Fe(II) minerals). Hydroxyl radicals were responsible for the degradation of DTPMP. The oxidation of DTPMP occurred with the
cleavages of both C-N and C-P bonds, forming phosphate and formate. The DTPMP structure has five phosphonate groups, and the current experimental data does not permit us to identify which specific location of phosphonate group degraded first. However, similar to the reaction scheme proposed by Nowack and Stone for the degradation of NTMP (nitrilotri(methylene)phosphonate), the simplified scheme proposed for the DTPMP degradation is shown in Figure 7.6. First, an one-electron abstraction from the nitrogen to ·OH forms a nitrogen-centered radical, and cleavage of the radical yields a carbon-centered radical followed by the release of phosphate. The methylene radical can further react with ·OH to form an iminium cation, which could be hydrolyzed to a new phosphonate and a formaldehyde. Oxidation of formaldehyde can form formate, as detected in our experiments. In addition, the methylene radical can be intercepted by O₂, and the intercepted radical can be further hydrolyzed to produce a formate and a new phosphonate.

Figure 7.6 Proposed mechanisms of DTPMP degradation by hydroxyl radicals generated through oxygenation of biotite.
7.3.3 Coupling of Biotite Reactivity and DTPMP Degradation at Different Temperatures

To further couple DTPMP degradation and biotite reactivity, DTPMP degradation experiments with biotite were conducted at 50 °C, 70 °C, and 95 °C. With biotite, at 50 °C, the evolutions of phosphate and formate concentrations were very slow, while faster increases of phosphate and formate concentrations were observed at higher temperatures (Figure 7.4). The results suggested that higher temperature favored DTPMP degradation with biotite. In addition to DTPMP degradation, biotite dissolution was monitored during the experiments.

Figure 7.7 SEM measurements of samples collected after 22 h reaction in 0.5 M DTPMP solution with biotite powders (A) and biotite flakes (B) at 102 atm of CO₂ and different temperatures (50, 70, and 95 °C). The EDX results of the spots indicated by the yellow and red boxes are shown in Figure 7-S2.
With DTPMP, increasing aqueous concentrations of K, Si, and Mg (Figure 7.3) were observed by ICP-OES at higher temperatures, indicating promoted biotite dissolution at higher temperatures. However, at 70 °C and 95 °C, the aqueous concentrations of Al and Fe first increased to around 90 µM and 150 µM, respectively, and then decreased. The decreases of Al and Fe concentrations were probably due to secondary precipitation of Al- and Fe-bearing secondary minerals. As confirmed by the SEM images in Figure 7.7A, after 22 h reaction at 70 °C and 95 °C, aggregated precipitates (indicated by the red box) were formed with sizes smaller than the original biotite powders (Figure 7-S1) were formed. The SEM images suggest both homogeneous precipitation in the reaction solution and heterogeneous precipitation on biotite surfaces. Characterized by EDX, the reacted biotite powders (yellow box in Figure 7.7A) had an elemental composition similar to unreacted biotite, but P was observed, indicating the adsorption of DTPMP or its degradation products. The secondary precipitates were abundant in P, Fe, and Al (Figure 7-S2). Although the secondary mineral phases were not the focal points of this study, as reported in a recent study of phosphate–biotite interactions, the homogeneous precipitates can be amorphous P, Fe, Al-bearing minerals, and the heterogeneous precipitates were probably strengite (FePO₄·H₂O), berlinite (AlPO₄), and gibbsite (Al(OH)₃). It was also possible that DTPMP or degraded DTPMP incorporated into the precipitates as organic templates for the secondary precipitation.

To better capture the effects of dissolution on biotite surface morphology changes, reacted biotite flakes were measured with SEM (Figure 7.7B). Consistent with our previous studies, cracks were formed on reacted biotite basal surfaces, and cracked layers bent outwards due to the adsorption of large DTPMP molecules. At elevated
temperatures, enhanced biotite dissolution kinetics induced deeper and more abundant cracks after biotite reacted with DTPMP (Figure 7.7B), exposing inner surface sites. The differences in the extent of secondary precipitation in the biotite powder and biotite flake reaction systems could result from biotite dissolution. Biotite powders possessed a much higher surface area than biotite flakes, which resulted in more biotite dissolution and higher saturations of secondary minerals. However, the trends of promoted biotite dissolution and the formation of deeper and more abundant cracks at higher temperatures should be the same for biotite powders and flakes.

To relate the DTPMP degradation with biotite dissolution, the following aspects were considered. First, faster biotite dissolution at higher temperatures could facilitate the generation of ROS, thus promoting DTPMP degradation. It has been reported that electron transfers between phyllosilicate structural Fe sites and redox-active substances can occur through both basal planes and edges. After reaction at higher temperatures, the deeper and more abundant cracks formed on biotite surfaces could expose more surface Fe(II) sites. These edge Fe(II) sites could react with O$_2$ to generate ROS to promote DTPMP degradation, confirmed by our observation (Figure 7.3). Second, a higher temperature could favor electron transfers within biotite structure and between Fe(II) sites and oxygen to produce ROS, which further reacts with DTPMP. The slow DTPMP degradation with biotite at 50 °C could result from limited electron transfers or limited reactive Fe(II) sites owing to slow biotite dissolution and less formation of cracks. Although original biotite contained mainly Fe(II) and there was limited Fe(II)-O-Fe(III) linkages for transferring electrons from inner to edge sites along the octahedral sheet. During the reaction, once surface Fe(II) sites were oxidized, inner Fe(II) could serve as electron pool to regenerate
the Fe(II) on the edges. Third, secondary precipitation could consume phosphate and cations, causing both DTPMP degradation and biotite dissolution reactions to proceed.

7.4 Environmental Implications

In this study, we provide new insights into the fate and transport of phosphonates used in engineered subsurface operations (high temperature and high pressure conditions) by studying the effects of different phyllosilicates on DTPMP phosphonate degradation and the mechanisms involved. The degradation of phosphonates will reduce their available concentrations in subsurface sites, thus affecting their performances in mineral scale inhibition. Moreover, significant secondary precipitation will clog pores, reducing the porosity and permeability of wellbores and reservoir rocks and affecting the transport of reactive fluids.

Phyllosilicates are abundant in shales, which are the main reservoirs for unconventional oil/gas recovery. The reported generation of reactive oxygen species by the interaction between oxygen and Fe(II) sites in phyllosilicates under subsurface relevant conditions suggests that we need to pay more attention to the role of Fe-bearing phyllosilicates, especially the contents and oxidation states of Fe in phyllosilicates. Although subsurface environments have low access to O₂, a small amount of O₂ can be imported to subsurface sites by surface water and groundwater interactions or by engineered subsurface processes. The generation of reactive oxygen species through oxygenation of Fe(II)-containing minerals may induce oxidative stress and affect the fate and transport of redox-active substances in subsurface sites. Additionally, Fe-reducing
bacteria can reduce Fe(III) in minerals to Fe(II),\textsuperscript{251-252} making Fe(III)-bearing phyllosilicates also effective in the transformation of redox-active substances.

**Acknowledgments**

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Supporting Information for Chapter 7

7-S1. Characterization of Fe(II) and Fe(III) in phyllosilicates

There was a caveat that using the digestion method, muscovite might not be fully digested due to its slow dissolution kinetics. The Fe content in muscovite might be underestimated. However, DTPMP degradation with muscovite was minor. Therefore, the general conclusion on the effects of muscovite on DTPMP degradation is valid.

7-S2. SEM measurements

Figure 7-S1 (A) SEM images of biotite, muscovite, and nontronite powders before reaction and (B) after 22 h reaction with 0.5 mM DTPMP at 95 °C and 102 atm of CO₂.
7-S3. EDX measurements

Figure 7-S2 EDX analyses by SEM of mineral samples after reaction at 50 °C (A), 70 °C (B), and 95 °C (C) in 0.5 mM DTPMP solution at 102 atm of CO$_2$. The corresponding images are shown in Figure 7.4A in the main text. M/Si is the Si atomic percent-normalized element content.
7-S4. pH\textsubscript{iep} measurements

Zeta (\(\zeta\)) potential measurements were conducted by dynamic light scattering (Malvern, Zetasizer, nano series) to determine the pH\textsubscript{iep} of biotite, muscovite, and nontronite. Mineral powders were dispersed in DI water and measured. The results are shown in Figure 7-S3. The measured pH\textsubscript{iep} for biotite is around 1.0, for muscovite is around 2.7–2.9. For nontronite, under the tested pH ranges of 1.7-6.0, it was negatively charged. Therefore, under our experimental pH condition of 3.2, all three phyllosilicates were negatively charged.

![Zeta potential measurements of phyllosilicate mineral suspension at different pH conditions.](image)

**Figure 7-S3** Zeta potential measurements of phyllosilicate mineral suspension at different pH conditions.
Chapter 8. Effects of Sulfate on Brine–Biotite Interactions under Subsurface Conditions: A Comparison with Other Inorganic/Organic Ligands

Abstract

To ensure the safety and efficiency of engineered subsurface operations, it is important to have a holistic understanding of the impacts of aqueous chemistries on brine–mineral interactions. In this study, using biotite as a model phyllosilicate, we investigated the effects of sulfate under subsurface relevant conditions (95 °C and 102 atm of CO$_2$). Sulfate at a concentration of 50 mM enhanced biotite dissolution by a factor of 1.35 by forming monodentate mononuclear complexes with biotite surface sites. Due to sulfate adsorption, biotite surfaces were altered to be slightly more hydrophilic. We compared the effects of various inorganic and organic ligands on brine–biotite interactions. Ligands that could form monodentate mononuclear (sulfate and phosphate) or bidentate mononuclear (oxalate) surface complexes promoted biotite dissolution, and bidentate complexes induced greater dissolution. In addition to surface complexation, aqueous complexation also occurred with DTPMP phosphonate, promoting biotite dissolution. Different from sulfate, acetate, and oxalate, the presence of phosphate and DTPMP significantly promoted secondary precipitation of Fe- and Al-bearing minerals. For all the inorganic and organic ligands examined, changes of biotite surface functional groups and surface charges due to ligand
adsorption were dominant over surface roughness in affecting biotite surface wettability. This study provides useful insights into the effects of brine chemistries on brine–mineral interactions for engineered subsurface operations.

8.1 Introduction

Subsurface energy sources, such as oil/gas fields and geothermal reservoirs, satisfy over 80% of total U.S. energy needs. Engineered subsurface operations, such as CO₂-enhanced conventional/unconventional oil/gas recovery, geologic CO₂ sequestration, and nuclear waste disposal, have received increasing attention to meet energy demands, mitigate global warming, and manage wastes. The field sites for these operations are usually deeper than 800 m, where the temperature and pressure can range from 31 °C to 110 °C and from 73.8 atm to 600 atm, respectively. The geophysical properties, such as wettability, porosity, and permeability, of reservoirs are important, because they affect the transport and distribution of related fluids that determine the safety and efficiency of the engineered subsurface operations. Mineral dissolution and secondary mineral precipitation are geochemical processes that can change the geophysical properties of reservoirs. These complex and interactive aspects underscore the need for a holistic understanding of geochemical processes of minerals under subsurface conditions.

Shales are abundant in reservoirs for subsurface engineered processes. Clay minerals (phyllosilicates), with a minimum mass fraction of about 40%, are main constituents of shales. Phyllosilicates have layered structures, containing framework cations occupying tetrahedral sheets and octahedral sheets, as well as interlayer cations to balance charge. During their dissolution, interlayer cations are released mainly through ion-exchange reactions with aqueous
protons or cations. Framework cations, on the other hand, are released through proton-mediated or ligand-mediated interfacial reactions. Aqueous species forming complexes with released metal ions can also mediate mineral dissolution by reducing the activity of aqueous metal ions. Moreover, metal ions released by mineral dissolution will change the saturation states in the solutions, leading to secondary mineral precipitation. In summary, the dissolution of phyllosilicates largely depends on the aqueous chemistry, and further affects secondary mineral precipitation.

Sulfate (SO$_4^{2-}$) is an abundant anion in formation brine, with concentrations ranging from 10 mM to 50 mM. Moreover, during co-injection of CO$_2$ and H$_2$S or SO$_2$, sulfate concentration can be much higher (800 mM). Under high temperature and high CO$_2$ pressure conditions, studies have reported that sulfate promotes anorthite dissolution and retards cement deterioration. However, the effects of sulfate on phyllosilicate dissolution have not been fully investigated yet. In addition, previous studies have shown that the introduction of seawater containing SO$_4^{2-}$ ions can modify oil-wet calcite to a more water-wet state, thus reducing the capillary barrier and improving the oil recovery efficiency in carbonate formations. Zhang et al. reported that the wettability modifying property of sulfate increased as the temperature increased. Still, information is limited on the influence of SO$_4^{2-}$ on the wettability of phyllosilicates, which are the main components of shales in unconventional oil/gas recovery, especially under relevant subsurface conditions.

Furthermore, other inorganic and organic ligands are also found in formation brines, such as phosphate (0–0.02 mM), acetate (16–250 mM), and oxalate (0–5 mM). Because supercritical CO$_2$ (scCO$_2$) is a good organic solvent, the concentrations of some organic compounds in brines (mainly formate and acetate) can increase even after CO$_2$ injection, as reported in a recent study on the Frio formation. In addition to these naturally existing aqueous
species, chemical additives are injected into subsurface sites during engineered operations.\textsuperscript{27-28} Among the chemical additives, scale inhibitors (e.g., phosphonates), with an average concentration of \( \sim 0.5 \) mM, are utilized to inhibit the formation of scale minerals, which can reduce the porosity and permeability of wellbores and cracked reservoir rocks, or block flow in production wells.\textsuperscript{29-33} Degradation of phosphonate scale inhibitors can also release phosphate and increase its concentration in brines to around 1–2 mM.\textsuperscript{48-49} Recently, we have reported the effects of phosphate, acetate, oxalate, and phosphonates on brine–biotite (a phyllosilicate) interactions.\textsuperscript{9,79,187} While we have a good amount of data on subsurface chemistry, we do not yet have a comprehensive and systematic understanding that will enable us to predict the effects of yet-unstudied ligands and aqueous chemistries.

Hence, the goal of this study was to provide a mechanistic understanding of the effects of sulfate on brine–mineral interactions and the subsequent wettability alterations under conditions relevant to subsurface environments. Biotite was used as a model phyllosilicate mineral. Further, we compared sulfate’s effects with those of other inorganic and organic ligands, by discussing the underlying mechanisms of their effects on mineral dissolution, secondary precipitation, and alterations of mineral surface morphology and wettability. The information presented in this study can be useful for better assessing the roles of a wide spectrum of aqueous ligands in subsurface brine in the geochemical processes of minerals, and their subsequent impacts on the wettability, porosity, and permeability of subsurface reservoirs.
8.2 Experimental Section

8.2.1 Chemicals and Minerals

All chemicals used were ACS grade or higher. To simulate subsurface brine conditions, sulfate solutions of different concentrations—0 (control), 1 mM, 10 mM, and 50 mM—were prepared in 1.0 M NaCl with deionized (DI) water (resistivity > 18.2 MΩ·cm, Barnstead Ultrapure Water Systems).

Biotite used in this study came from Bancroft, Ontario, Canada, and was purchased from Ward’s Natural Science. The elemental composition of biotite was K_{0.91}Na_{0.08}Ca_{0.005}(Mg_{0.57}Mn_{0.02}Fe_{0.37}Ti_{0.04})_3(Al_{1.00}Si_{3.00})O_{10}(F_{0.51}(OH)_{0.49})_2, analyzed by X-ray fluorescence (XRF) (Table 2.1). Biotite flakes freshly cleaved along {001} basal planes were cut into 2.0 cm × 0.8 cm rectangles with a thickness of 80 ± 10 μm (measured with a Vernier caliper). The biotite flakes were sonicated successively in acetone, ethanol, and isopropanol for 5 mins each to remove organic contaminants, then rinsed with DI water and dried with high purity nitrogen gas. The prepared biotite flakes were stored in dust-free tubes for further dissolution experiments.

8.2.2 High Temperature and High Pressure Reactions

Laboratory biotite dissolution experiments were conducted in a 300 mL high-temperature and high-pressure reactor (Parr Instrument Co., IL), as used in our previous studies (Figure 2.1). To mimic field site pressure (73.8–600 atm) and temperature (31–110 °C) conditions and to obtain results comparable with previous reports, the experimental pressure was 102 atm CO₂ and the temperature was 95 °C. The initial in situ pH of the control solution at
the experimental pressure and temperature conditions was around 3.16, calculated by Geochemist’s Workbench (GWB, Release 8.0). Hence, the pH of the sulfate solutions was adjusted to give the systems the same initial \textit{in situ} pH as the control system at 95 °C and 102 atm CO₂. Due to the high salinity (1.0 M NaCl) in the solutions, the additions of hydrochloric acid (HCl) and sodium hydroxide (NaOH) during pH adjustment did not much affect the ionic strength. Duplicate biotite flakes were reacted in the prepared solutions for desired time intervals (3, 8, 22, 70, and 96 h). Triplicate experiments were conducted. The experiments provided information on brine–biotite interactions in the early period of engineered subsurface operations.

After the reactions, the reactor was slowly degassed by releasing the pressure valve and allowed to cool. The reaction solutions were then filtered through 0.2 μm polypropylene membranes and acidified in 1% trace metal nitric acid (HNO₃). The aqueous solutions were analyzed with inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 7300 DV) to determine the dissolved ion concentrations, and measured with ion chromatography (IC, Thermo Scientific Dionex ICS-1600) for the residual sulfate concentrations in the solutions. Sulfate adsorption in each system was calculated as the difference between the initial and residual sulfate concentrations, normalized by the initial biotite surface area. The pH values after 96 h reaction were calculated by taking ICP-OES and IC results as input for GWB calculations.

\textbf{8.2.3 Characterization of Surface Morphology of Reacted Biotite}

The reacted biotite flakes were rinsed with DI water, dried with high purity nitrogen, and then used for further characterizations. For surface morphology, the reacted biotite flakes were mounted on steel pucks and placed on a sample stage, then measured with atomic force microscopy.
(AFM, Nanoscope V Multimode SPS, Veeco). AFM measurements were conducted under ambient conditions in contact mode. Using nonconductive silicon nitride probes (tip radius of 10 nm, DNP-S10, Bruker), the biotite basal surface was scanned at a rate of 0.999 Hz and a deflection setpoint of 1.975 V. The collected AFM images were analyzed with Nanoscope software (v7.20). Statistical information about the height, crack depth, and root-mean-square surface roughness \( R_q \) was obtained through the analyses. More details can be found in 8-S1.

8.2.4 Measurement of Contact Angles

Wettability alteration is indicated by changes in contact angles. Under ambient conditions, we used a contact analyzer (Surface Electro Optics, Phoenix 300) to measure contact angles of biotite samples reacted in the high temperature and high pressure systems. Images of droplets of DI water placed on biotite basal surfaces were taken with a high-resolution camera. At least six measurements were made on every biotite sample. Contact angles were then obtained by analyzing the images.

8.2.5 Fourier Transformation Infrared (FTIR) Spectroscopy Analyses of Sulfate Complexation

To investigate the types of sulfate–biotite surface complexes, attenuated total reflectance (ATR)-FTIR spectra were collected under ambient conditions using a Thermo Scientific Nicolet iS10 spectrometer with a horizontal Ge ATR crystal. Using the method described in Chapter 3, biotite particles with an average size of about 100 nm, determined by dynamic light scattering, were deposited onto the Ge crystal and allowed to dry. Solutions were prepared of (a) 1 M NaCl, (b) 1 M NaCl + 1 mM sulfate, (c) 1 M NaCl + 10 mM sulfate, and (d) 1 M NaCl + 50 mM sulfate.
All three solutions had an initial pH of 3.16, the same value as the initial pH of the high temperature and high pressure experiments. Next, 1 mL of the prepared solution was added to the crystal and allowed to contact the dried biotite particle film. Four hundred scans were collected, with a resolution of 1 cm⁻¹. Then, the spectrum of biotite contacting solution (a) was used as a background and subtracted from the spectra of biotite contacting solutions (b), (c), and (d).

8.3 Results and Discussion

8.3.1 Effects of Sulfate on Biotite Dissolution and Surface Morphology Evolution

The effects of sulfate on the evolutions of aqueous cation concentrations in the reaction systems are shown in Figure 8.1. Regarding interlayer K⁺, similar aqueous concentrations were observed in all four reaction solutions. It is known that the release of interlayer cations (K⁺ in the case of biotite) is through ion-exchange reactions with cations in the solution.²⁵⁶ In the reaction solutions, the ionic strength was controlled to be around 1.0 M, and the initial in situ pH value was adjusted to be 3.16. The final pH values of the solutions after reaction with biotite for 96 h, calculated by GWB, were very close, with values around 3.39 for the control, 3.42 for 1 mM sulfate, 3.46 for 10 mM sulfate, and 3.36 for 50 mM sulfate. Please note, during the thermodynamic calculations, the calculated pH was very sensitive to the input of sulfate concentrations. Considering the error bars of sulfate concentration measurements, we assumed that there are no big differences in the pH values calculated for the four systems. The concentration levels of H⁺ and Na⁺ in all the reaction systems were close, resulting in similar extents of ion-exchange
reactions between interlayer K$^+$ and cations in the solutions. Hence, compared with the control, sulfate did not affect the released K$^+$ concentrations in the solutions.

However, the aqueous concentrations of the framework Si, Mg, Fe, and Al cations were affected by sulfate. The effects of low sulfate concentrations (1 mM and 10 mM) were not discernable from control experiments, while the presence of 50 mM sulfate promoted the release of framework cations by a factor of around 1.35. The pH of the reaction systems was close; hence, the proton-mediated dissolution reaction was not the responsible dissolution pathway. Interestingly, in a recent study, Min et al. reported that 50 mM sulfate enhanced the dissolution of anorthite (CaAl$_2$Si$_2$O$_8$) by with a factor of 1.36, a value very close to our finding. They commented that aqueous complexation could not explain their observations. In our experimental system, according to thermodynamic calculations using GWB, the main aqueous species of sulfate was SO$_4^{2-}$, and its aqueous complexation with metal ions was very weak due to low stability constants. Therefore, in this study, aqueous complexation was also not the mechanism for the promotion effects of 50 mM sulfate. Min et al. further explained that the formation of inner-sphere monodentate complexes between sulfate and the aluminum sites on anorthite surfaces was responsible for the enhancement effects of sulfate on anorthite dissolution. Thus, we hypothesized that the formation of complexes between sulfate and biotite surface sites could also occur to promote biotite dissolution in our reaction systems.
Figure 8.1 Aqueous concentrations of Si, Al, Fe, Mg, and K from dissolution of biotite at 95 °C and 102 atm CO$_2$, with an ionic strength of around 1.0 M and an initial pH of 3.16, in 0, 1, 10, and 50 mM sulfate solutions. Error bars are the standard deviations of duplicate samples in triplicate experiments.

8.3.2 Sulfate Complexation and Adsorption on Biotite Surfaces

Figure 8.2 ATR-FTIR spectra of biotite contacted with different concentrations of sulfate. The spectrum of biotite contacted with 1 M NaCl was used as background. Inset: Amount of sulfate adsorbed onto biotite after 22 h reaction with different initial concentrations of sulfate under 95 °C and 102 atm CO$_2$. 
To explore our hypothesis of sulfate surface complexation with biotite, ATR-FTIR spectra of sulfate contacted with biotite are shown in Figure 8.2. Although aqueous sulfate has an asymmetric stretching at 1100 cm\(^{-1}\), we observed that the band centered at 1100 cm\(^{-1}\) was broad between 1050 cm\(^{-1}\) and 1140 cm\(^{-1}\). Serna et al. reported this feature corresponds to monodentate mononuclear surface complexes between sulfate and Al oxide. For ligand-mediated dissolution, monodentate mononuclear surface complexes can promote mineral dissolution through polarizing metal-oxygen bonds and facilitate the detachment of surface metal species. In addition, we observed a higher intensity of monodentate mononuclear surface complexes in the presence of 50 mM sulfate than 1 mM and 10 mM sulfate, indicating more significant surface complexation with 50 mM sulfate. Correspondingly, after 8 h of high T/P reaction, higher sulfate adsorption was observed as the initial sulfate concentrations increased (inset in Figure 8.2). The surface complexation with 1 mM and 10 mM sulfate was not sufficient to induce observable promotion of biotite dissolution, and the enhancement effects were more obvious with 50 mM sulfate, as seen in Figure 8.1. Note that binuclear surface complexes are not expected on biotite. Due to the Al avoidance principle, there are no adjacent Al sites to form binuclear surface complexes. The peak at around 1025 cm\(^{-1}\) was attributed to Si-O bands of biotite, which were not fully subtracted.

8.3.3 Effects of Sulfate on Biotite Surface Morphology and Wettability Alterations

The presence of different concentrations of sulfate did not significantly affect the morphological evolutions of reacted biotite basal surfaces, measured by AFM and shown in Figure 8-S1 and Figure 8.3. Fibrous precipitates, identified in a previous study to be fibrous illite formed
by oriented aggregation of small hexagonal nanoparticles on control samples, was also observed on biotite basal surfaces after 3 h of reaction with sulfate (Figure 8-S1). In addition, after reactions of 22 h and longer, cracks were formed on reacted biotite basal surfaces, as a result of ion-exchange reactions of aqueous Na\(^+\) with biotite interlayer K\(^+\), dissolution of framework cations, and CO\(_2\) intercalation. Figure 8-S2A shows statistical data on crack depths, found by taking the average of 80 spots where the cracks were located in four representative AFM images. Consistent with ICP-OES results of indistinguishable biotite dissolution among the control, 1 mM sulfate, and 10 mM sulfate systems (Figure 8.1), the depths of cracks formed were close after 22 and 44 h reactions. After a longer reaction time of 70 h with 50 mM sulfate, the cracks formed on biotite basal surfaces were slightly deeper, suggesting more biotite dissolution (Figure 8.1). We should note that detachments of surface cracked layers into the solutions after 96 h reactions made the crack depths observed smaller than those on 70 h samples. The changes of surface roughness of reacted biotite samples over time were also analyzed (Figure 8-S2B). Due to the formation of fibrous illite and cracks on biotite, the surface roughness increased over time. However, among the control and sulfate samples, the surface roughness of reacted biotite samples was almost the same. This observation was as expected, because no big differences in surface morphologies were observed for samples reacted in the four systems.
Figure 8.3 Height mode AFM observations of biotite basal surfaces after reaction at 95 °C and 102 atm CO₂ with different aqueous chemistries. The AFM images are 50 µm × 50 µm. The height scale is 60 nm for images A, B, C, D, E-8 h, and F-8 h, is 100 nm for E-72 h, and is 200 nm for F-70 h. The different height scales show the results more clearly. Inset in F-70 h is an SEM image of the corresponding sample. The arrows in the same colors point to similar surface features.

Figure 8.4 Contact angles of biotite basal surfaces after reactions in solutions of various aqueous chemistries over time at 95 °C and 102 atm of CO₂. The error bars are standard deviations of six measurements of duplicate samples in triplicate experiments.

Furthermore, the wettability alterations of reacted biotite basal surfaces were characterized and are shown in Figure 8.4. The contact angles for samples reacted in 1 mM sulfate systems were close to those of control samples (27°). However, the contact angles for samples reacted in 10 mM
and 50 mM sulfate were about 5° lower than control samples, indicating enhanced biotite surface wettability. The alterations of biotite surface wettability by sulfate could be attributed to sulfate surface adsorption. As shown in the inset in Figure 8.2, the amount of adsorbed sulfate was much smaller in the 1 mM sulfate system than in the 10 mM and 50 mM sulfate systems. Therefore, biotite reacted with 1 mM sulfate did not show different surface wettability from the control samples. In the 10 mM and 50 mM sulfate systems, the higher amounts of sulfate adsorption could expose hydrophilic functional groups on biotite surfaces.²⁶⁸–²⁶⁹ Additionally, the main aqueous sulfate species under the experimental pH was SO₄²⁻. Adsorption of SO₄²⁻ could also make biotite surfaces more negatively charged. These two aspects of sulfate adsorption resulted in lower contact angles of reacted biotite samples and enhanced their surface wettability. It has been reported that surface roughness contributed to more hydrophilic biotite surfaces.¹⁶⁸ As shown in Figure 8-S2B, after the same reaction times, the surface roughness values were close for biotite samples in all the four systems. Therefore, surface roughness was not the dominant mechanism for the sulfate effects on biotite wettability alterations in this study.

8.3.4 A Comparison of Sulfate Effects with Those of Other Inorganic/Organic Ligands

Figure 8.5 shows sulfate effects compared with those of other inorganic/organic ligands, discussed in previous chapters, on biotite dissolution and secondary precipitation. The relative K, Si, and Fe scale indicates the ratios of cation concentrations in the corresponding systems with various aqueous species to those in the control systems, all for 70 h. Mediated by ion-exchange reactions and as a result of controlled ionic strengths and the initial pH, interlayer K⁺ ratios were
almost all close to 1, indicating no influences of sulfate, phosphate, acetate, and DTPMP (diethylenetriamine penta(methylene) phosphonate) on K⁺ dissolution. The 10 mM oxalate system was an exception, with a ratio of 0.75.

The dissolution of framework cations is through proton-mediated or ligand-mediated reactions. For framework Si, the ratios were greater than 1 with 50 mM sulfate, 10 mM phosphate, 10 mM oxalate, and 0.5 mM DTPMP, indicating their enhancement effects on biotite dissolution. Notably, oxalate significantly promoted biotite dissolution, suggested by the higher ratios of Si and Fe. The promoted mineral dissolution could create void spaces and affect reservoir porosity. In the 10 mM oxalate system, the enhanced biotite dissolution released high concentrations of framework cations in solution, contributed to higher a final pH than the control, and inhibited the release of interlayer K.⁷⁹ We identified monodentate mononuclear complexes between sulfate/phosphate and biotite surface sites, and the surface complexes formed between oxalate and biotite were bidentate binuclear, which more strongly promoted biotite dissolution. Aqueous complexation also played a role in the DTPMP system, facilitating biotite dissolution.

For Fe, ratios greater than 1 were observed with 50 mM sulfate and 10 mM oxalate. Although 10 mM phosphate and 0.5 mM DTPMP enhanced biotite dissolution, as suggested by the Si findings, the ratios for Fe were smaller than 1. The differences among Fe ratios in these sulfate, oxalate, phosphate, and DTPMP systems resulted from their propensity to precipitate with Fe. Fe-bearing phosphate/phosphonate minerals, with solubility product constants (K_{sp}) lower than the order of 10^{-19},⁸⁹,¹⁹⁸-¹⁹⁹ are much less soluble than Fe-sulfate/oxalate. After the reactions with phosphate and DTPMP, we identified precipitation of strengite (FePO₄·2H₂O) on biotite basal surfaces, and detected amorphous Fe-bearing minerals in the solutions. The precipitation of these Fe-bearing minerals led to Fe ratios smaller than 1 in the phosphate and DTPMP systems. Al-
bearing secondary precipitates were also observed in the phosphate and DTPMP systems. The significant formation of secondary minerals may plug pores in reservoir rocks, thus affecting their porosity and permeability. In the 10 mM acetate system, we observed Si and Fe ratios slightly lower than 1. Acetate slightly inhibited biotite dissolution through adsorption of acetic acid onto surface Si and Al sites, influencing the protonation of biotite surfaces.

![Figure 8.5](image)

**Figure 8.5** A comparison of sulfate effects with phosphate, acetate, oxalate, and DTPMP on cation concentrations during biotite dissolution at 95 °C and 102 atm CO₂.

As a result of altered biotite dissolution and secondary precipitation, the changes in biotite surface morphology were different. With 10 mM phosphate, 10 mM oxalate, and 0.5 mM DTPMP, formation of cracks was facilitated by the enhanced biotite dissolution, observed within 8 h of reaction (Figure 8.3). The cracks on biotite surfaces made fibrous illite less observable (Figure 8.3C, E, F-8 h). Significant surface precipitation of Fe- and Al-bearing minerals was observed in the 10 mM phosphate and 0.5 mM DTPMP samples, resulting in rough surfaces (Figure 8.3C and 3F-70 h). Different from sulfate, phosphate, acetate, and oxalate, surface adsorption of large DTPMP molecules made the cracked biotite layers bend outwards (inset in Figure 8.3F-70 h).

We previously reported that salinity-induced chemical reactions altered biotite surface wettability, as a result of changes in surface roughness, surface charge, and surface functional
groups. Here, we compare of biotite surface wettability alterations after reaction with different aqueous inorganic/organic species, with the results shown in Figure 8.4. Sulfate, phosphate, oxalate, and DTPMP enhanced biotite surface wettability, with lower contact angles observed. The adsorption of these chemical species, exposing hydrophilic functional groups on biotite surfaces and creating a more negative surface charge, is the dominant over surface roughness in enhancing surface wettability. Also, XPS O 1s results showed that significant biotite dissolution, promoted by oxalate, induced a higher density of hydroxyl groups on reacted biotite surfaces (Table 8-S1). The increase of hydroxyl groups could contribute to the enhanced biotite surface wettability by oxalate.\(^{168}\) Differently, 10 mM acetate induced higher contact angles than control sample, suggesting that biotite was altered to be more hydrophobic. Acetic acid was the dominant aqueous species in the 10 mM acetate system under the experimental conditions, and its adsorption would orient the carboxylic groups to point toward the mineral surface and leave a hydrophobic methyl group in the outer surface.

Table 8.1 A summary of field concentrations of various inorganic/organic ligands, and their interactions with biotite and consequent effects on dissolution, precipitation, and wettability.

<table>
<thead>
<tr>
<th>Field concentration (mM)</th>
<th>Sulfate</th>
<th>Phosphate</th>
<th>Acetate</th>
<th>Oxalate</th>
<th>Phosphonate (DTPMP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interaction</td>
<td>surface complexation</td>
<td>monodentate mononuclear surface complexation</td>
<td>surface adsorption to Si &amp; Al</td>
<td>bidentate mononuclear surface complexation</td>
<td>aqueous complexation &amp; surface complexation</td>
</tr>
<tr>
<td>Dissolution</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↑↑↑</td>
<td>↑↑↑</td>
</tr>
<tr>
<td>Precipitation</td>
<td>--</td>
<td>↑↑↑</td>
<td>↑</td>
<td>↑↑</td>
<td>↑↑</td>
</tr>
<tr>
<td>Wettability</td>
<td>↑</td>
<td>↑↑↑</td>
<td>↓</td>
<td>↑↑</td>
<td>↑↑</td>
</tr>
</tbody>
</table>

Note: Different pH conditions may affect the interactions between inorganic/organic ligands with biotite. The tabulated information was summarized from experiments with pH values lower than 4.5.
8.4 Environmental Implications

In this study, we report the effects of sulfate on brine–biotite interactions under high temperature and high pressure conditions relevant to engineered subsurface operations. A sulfate concentration of 50 mM promoted biotite dissolution by a factor of around 1.35, mainly through monodentate mononuclear surface complexation. Sulfate adsorption slightly enhanced biotite surface wettability. In addition, we provide a comparison of sulfate effects with those of other inorganic/organic ligands (Table 8.1), which showed different effects on biotite dissolution. Ligands that could form monodentate mononuclear surface complexes (sulfate and phosphate) or bidentate mononuclear surface complexes (oxalate) promoted biotite dissolution, and the latter configuration induced greater promotion. DTPMP, a ligand with the highest number of functional groups among those studied, promoted biotite dissolution through both aqueous complexation and surface complexation. Different from sulfate, acetate, and oxalate, the presence of phosphate and DTPMP, both having phosphate functional groups, significantly promoted secondary precipitation of Fe- and Al-bearing minerals. For all the inorganic and organic ligands, biotite surface wettability was altered more by surface adsorption changing surface functional groups and surface charges than by changes in surface roughness.

Subsurface brine contains a wide spectrum of inorganic and organic ligands. The results summarized in this study suggest that, as a starting point, we can examine the functional groups in the ligands and consider their general effects on mineral dissolution and secondary precipitation. The extents of these dissolution and precipitation reactions will further affect the porosity and permeability of subsurface reservoirs. By analyzing the possible functional groups exposed on mineral surfaces as a result of adsorption of aqueous chemical species, we can also obtain a first
understanding of their effects of mineral wettability alterations. We should also note that coexisting ligands may compete with each other to suppress effects of other ligands, or they may show synergetic effects on the geochemical reactions of minerals. Future studies are needed to investigate multi-ligand systems. Porosity, permeability, and wettability are important parameters impacting the transport and distribution of fluids at subsurface sites. Therefore, the study can provide useful insights into the effects of brine chemistries on brine–mineral interactions, and ultimately can benefit engineered subsurface operations.

Acknowledgments

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Supporting Information for Chapter 8

8-S1. AFM measurements

Root-mean-square surface roughness \( (R_q) \) is defined as
\[
R_q = \sqrt{\frac{1}{L} \int_0^L Z^2(x) \, dx},
\]
where \( Z(x) \) is a function that describes the surface profile analyzed in terms of the height \( (Z) \) and position \( (x) \) of the sample over the evaluation length \( L \). We used this definition as an indicator of surface roughness. For each sample, at least four locations on the sample surface were measured to determine the roughness. The depth of the cracks in sample surfaces were also measured from the AFM images by taking the average of 20 spots from four representative AFM images.

![AFM images](image)

**Figure 8-S1** Height mode AFM images of biotite basal surfaces after reaction with different concentrations of sulfate at 95 and 102 atm CO\(_2\). The height scale is 60 nm.
Figure 8-S2 (A) Statistical crack depth and (B) roughness of biotite basal surfaces after reaction with different concentrations of sulfate at 95 and 102 atm CO₂.

8-S2. XPS measurements

X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, Ulvac-PHI with monochromatic Al Kα radiation (1486.6 eV)) was used to investigate the surface functional groups of oxygen on biotite. The C 1s (284.8 eV) spectrum was taken as the energy reference. Narrow scans of O 1s spectra were analyzed with Shirley background subtraction. The pass energy for the narrow scans was 23.5 eV. The fittings of O 1s photolines were conducted based on the Gaussian-Lorentzian algorithm, using Multipak V 7.0.1 (Ulvac-PHI, Inc.). Both bridging oxygens (T–O–T, T: tetrahedral site) and terminal oxygens (T–OH) are present on the surface of aluminosilicates. Water molecules are also on the mineral surface. In XPS analyses, the oxygen peak in the range of 528-536 eV was deconvoluted. The peak with a binding energy of around 530.0 eV was assigned to bridging oxygen (O²⁻), the peak with a binding energy of 531 eV was assigned to hydroxyl oxygen (–OH), and the peak with a binding energy of 533 eV was assigned to water molecules (H₂O), according to the literature. Next, the percentages of oxygen species at the biotite surface after reaction under 95 °C and 102 atm CO₂ were obtained.
<table>
<thead>
<tr>
<th>Condition</th>
<th>$O^2-$ (%)</th>
<th>OH (%)</th>
<th>H$_2$O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M NaCl</td>
<td>5.5</td>
<td>89.2</td>
<td>5.3</td>
</tr>
<tr>
<td>1 M NaCl+10 mM oxalate</td>
<td>5.4</td>
<td>91.2</td>
<td>3.4</td>
</tr>
<tr>
<td>1 M NaCl+10 mM acetate</td>
<td>6.2</td>
<td>87.5</td>
<td>6.3</td>
</tr>
</tbody>
</table>
Chapter 9. Conclusions and Future Directions

9.1 Conclusions

To enable safer and more efficient energy-related engineered subsurface operations, in this dissertation we investigated coupling the geochemical reactions of clay minerals with the resulting changes of their geophysical properties, which are key to the trapping of CO₂ and transport of related fluids. Specifically, we examined the effects of subsurface-relevant aqueous chemistry conditions, i.e., salinity, organic and inorganic oxyanions, and phosphonate-based scale inhibitors, on brine–clay mineral interactions. Furthermore, we linked the consequent alterations of geophysical properties, focusing on wettability, to the brine–clay mineral interactions. The findings on the coupling of geochemical reactions and geophysical properties of clay minerals will benefit more sustainable engineered subsurface operations.

Task 1 focused on investigating salinity-induced chemical reactions and the wettability alterations of biotite under subsurface relevant conditions. Biotite dissolution and surface wettability were characterized after reactions in solutions of different salinities. Surface property changes linked wettability alteration with chemical reactions of biotite. Higher salinity promoted more biotite dissolution, resulting in biotite surfaces with increased roughness, more negative charge, and higher densities of hydroxyl groups. All these changes in surface properties contributed to enhancing biotite surface wettability. The findings from Task 1 provide important insights into coupling chemical reactions and wettability alterations of minerals at subsurface sites.

Task 2 aimed at investigating brine–clay mineral interactions in the presence of organic and inorganic oxyanions and clarifying the mechanisms of their effects. First, the effects of short-
chain carboxylic acid anions and the distinctive reactivities of biotite edge and basal planes were examined. Acetate and oxalate affected biotite dissolution and secondary mineral precipitation through different mechanisms. Acetate slightly inhibited biotite dissolution and promoted secondary precipitation through pH-induced aqueous acetate speciation and subsequent surface adsorption. However, oxalate significantly enhanced biotite dissolution by forming bidentate mononuclear surface complexes. For the first time, we identified that oxalate increases the relative reactivity ratio of biotite edge surfaces to basal surfaces by selectively attacking the edge surface sites. Next, we examined the effects of anionic inorganic phosphate on biotite dissolution and secondary mineral precipitation, and the consequent wettability alterations. Biotite dissolution experiments were conducted without and with the presence of different concentrations of phosphate. Phosphate at a concentration of 10 mM enhanced biotite dissolution far more than lower phosphate concentrations (0, 0.1, and 1 mM). However, in all the phosphate systems, secondary precipitation of Fe- or Al-bearing minerals was promoted on biotite surfaces and in the reaction solutions. Such significant precipitation may impact the porosity and permeability of reservoir rocks. Moreover, we identified that phosphate adsorption onto biotite surfaces made them more hydrophilic. Therefore, in addition to the surface property changes discussed in Task 1, adsorption of chemicals in brine onto mineral surfaces is important in the alteration of mineral wettability.

Task 3 elucidated the interactions between clay minerals and organic phosphonates, which are injected into subsurface sites as scale inhibitors during engineered operations. We first investigated the effects of DTPMP (a model phosphonate) concentrations (0–1.0 mM) on brine–biotite interactions and on biotite’s wettability alteration due to the interactions. DTPMP enhanced biotite dissolution through both aqueous and surface complexations, with more significant effects
at higher concentrations. Homogeneous precipitation in the solutions and heterogeneous precipitation on the reacted biotite surfaces of Fe- and Al-bearing minerals were also enhanced with DTPMP. After longer reaction time (44 h), in the presence of 1.0 mM DTPMP, significant surface precipitation and less detachment of cracked layers inhibited further biotite dissolution. Like phosphate, we observed that DTPMP adsorption made the reacted biotite surfaces more hydrophilic due to the exposure of hydroxyl groups on biotite surfaces. Second, we compared the effects of different phosphonates on brine–biotite interactions and their impacts on biotite surface wettability. The effects of phosphonates were structure-dependent. IDMP with the fewest phosphonate functional groups promoted biotite dissolution through surface complexation, while DTPMP promoted biotite dissolution mainly through aqueous complexation. All the phosphonates enhanced secondary precipitation of P-, Fe-, and Al-bearing minerals, while their morphology, distribution, and phases were affected by the structures of the phosphonates. The phosphonates showed no distinguishable enhancing effects on biotite surface wettability, indicating that adsorption of only a small amount of phosphonate was sufficient to enhance wettability. Third, the chemical stability of phosphonates affected by the reactivity of clay minerals was investigated. Clay minerals with different Fe contents and oxidation states induced DTPMP degradation to different extents. Biotite (Fe(II)-rich) significantly promoted DTPMP degradation by reactive oxygen species generated through the reduction of molecular oxygen with Fe(II) sites in biotite, while muscovite (Fe-poor) and nontronite (Fe(III)-rich) did not show obvious effects. The outcomes from Task 3 broadened our understanding of the impacts of phosphonate chemical additives on the geochemical reactions of clay minerals, and the fate and transport of phosphonates at subsurface sites.
To conclude, we have explored the interactions between brine and clay minerals under various aqueous chemistry conditions and elucidated the underlying mechanisms. We have also successfully coupled the alterations of mineral wettability to brine–mineral interactions by considering surface physico-chemical property changes and chemical adsorption. These results will advance our understanding of the geochemical and hydrogeophysical processes of rocks and minerals in engineered subsurface operations.

9.2 Recommended Future Directions

Our new findings have provided an improved understanding of brine–mineral interactions in various aqueous chemistry conditions relevant to engineered subsurface operations. Further, focusing on wettability, we have identified the interplays between geochemical reactions and the geophysical properties of minerals. Inspired by this work, future research directions are recommended.

First, more attention is needed on the anisotropic structure of clay minerals. The properties of the basal and edge surfaces of clay minerals are different, with valence-saturated oxygen on the basal surfaces and high energy broken bonds terminated by valence-unsaturated oxygens present at edge surfaces. As a result of the distinctive properties of edge and basal surfaces, their preferences for CO$_2$ or water differ. Considering the different reactivities of edge and basal surfaces and the effects of chemical reactions on wettability alterations, the alteration of edge surfaces caused by chemical reactions will be more significant. Thus, the extent of subsequent wettability changes will be different. Examining the anisotropic wettability behavior of the basal
and edge surfaces of clay minerals can be useful in understanding the flow of related fluids in shale reservoirs.

Second, in addition to the wettability alteration described in this work, another future research can pursue the relationships between the chemical reactions of minerals and their porosity, permeability, and mechanical properties. Mineral dissolution will create void spaces, and secondary mineral precipitation will occupy pore spaces or plug pore throats. During hydraulic fracturing, shale reservoirs are cracked, and porosity and permeability are key to the flow and transport of the oil and gas. However, as discussed in this study, phosphonates that are injected to inhibit mineral scale formation promote the precipitation of Fe- and Al-bearing minerals. Information is limited on the actual effects of phosphonate on the porosity and permeability changes of reservoir rocks. To evaluate the performance of phosphonate scale inhibitors in subsurface sites, quantitative studies are needed on the influence of phosphonate-induced precipitation on shale porosity and permeability alterations. Moreover, it has been demonstrated that the clay mineral mass fraction (X_{clay}) is a very important variable that controls the properties of shale formations, and there is a sharp threshold at X_{clay}~1/3 that separates shales as sealing (X_{clay}>1/3) or brittle (X_{clay}<1/3). The same report pointed out that dissolution of carbonate minerals will increase X_{clay} and thus improve the seal integrity of caprocks. As discussed in this dissertation, dissolution of clay minerals occurs under subsurface relevant conditions, which may reduce the clay fraction in rock matrix and degrade the mechanical properties of caprocks. Hence, we also need to characterize the effects of geochemical reactions of clay minerals on the alterations of mechanical properties.

In addition, investigations are recommended to scale up the reaction systems. We have provided small scale (nano- and micro-) findings about the effects of chemical reactions on
wettability alteration, which can be good starting points to understand the large-scale processes. However, more efforts are needed to scale up these findings. Three aspects of scaling up can be considered: from a single-mineral system to a rock matrix, from simplified aqueous chemistry parameters to multiple aqueous species, and from short-term reaction to long-term storage. Rock matrix contains many types of minerals, e.g., shales contain various phyllosilicates along with quartz, feldspars, and calcite, exhibiting different reaction rates. It is important to link the information on geochemical reactions of biotite provided in this study to other phyllosilicates sharing similar structures, an effort that will ultimately benefit the broad understanding of shales. Moreover, in the rock matrix, some minerals will dissolve faster, and some minerals will be more stable. Dissolution of reactive minerals in rock matrix will lead to preferential flow pathway, thus changing geophysical properties. In addition, the brine at subsurface sites is a mixture of various aqueous species having different effects on mineral chemical reactions. For example, as we presented, oxalate significantly promotes mineral dissolution, but phosphate and phosphonates strongly precipitate with Fe and Al. The co-existence of oxalate and phosphate or phosphonates will affect mineral dissolution and secondary precipitation and the subsequent geophysical property alteration in different ways. Furthermore, studies such as site observation or modeling are needed to link the short-term experimental results with long-term storage. Short-term experimental results provide useful kinetic and thermodynamic data for understanding the long-term behavior.

In summary, the studies presented in this dissertation coupled geochemical reactions and the geophysical properties of clay minerals under conditions relevant to engineered subsurface operations. The outcomes provide a mechanistic basis for future studies on the geochemical processes of minerals and hydrogeologic processes of related fluids. Ultimately, this research will benefit designing safer and more efficient energy-related engineered subsurface operations.
References


Curriculum Vitae

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EDUCATION

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RESEARCH EXPERIENCE

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- Elucidated the effects of aqueous chemistry conditions (i.e., salinity, organic and inorganic oxyanions, and phosphonate scale inhibitors) on brine–clay mineral interactions under conditions relevant to enhanced oil recovery, and identified the interplays between geochemical reactions and geophysical properties of clay minerals
- Developed multidisciplinary instrumental skills, including AFM, SEM, FTIR, ICP-OES, ICP-MS, DLS, UV-Vis, IC, XRD, BET, TOC, TEM, X-ray microtomography, (GI)SAXS
- Participated in collaborative research projects with Dr. Laura Nolte (Purdue University) on calcium carbonate precipitation in fractures

Visiting Student, Energy Geosciences Division, Lawrence Berkeley National Laboratory, 2015.5

- Conducted high-temperature and high-pressure wettability test, in collaboration with Dr. Jiamin Wan and Dr. Yongman Kim
HONORS AND AWARDS

- Doctorate Student Research Award, Washington University in St. Louis 2018
- Student Travel Award in Geochemistry Division, American Chemical Society 2018
- Student Travel Grant from the North Central Section of the Geological Society of America to attend GSA North-Central Section Meeting 2016
- ENVIRSAN Scholarship from Washington University in St. Louis 2012
- Undergraduate Student with Honor, Tsinghua University, China 2012
- National Encouragement Scholarship from Ministry of Education, China 2010, 2011
- First-class Academic Scholarship from Tsinghua University, China 2009

PUBLICATIONS


CONFERENCE PRESENTATIONS

1. **Lijie Zhang** and Young-Shin Jun, Redox Degradation of DTPMP Phosphonate with Fe-bearing Phyllosilicates under Subsurface Conditions, The 255$^{th}$ American Chemical Society National Meeting & Exposition, New Orleans, Louisiana. 2018

2. **Lijie Zhang** and Young-Shin Jun, Effects of Phosphonates on Brine–Biotite Interfacial Reactions under Conditions Relevant to Energy-related Subsurface Operations, The 255$^{th}$ American Chemical Society National Meeting & Exposition, New Orleans, Louisiana. 2018

3. **Lijie Zhang**, Doyoon Kim, and Young-Shin Jun, Effects of Diethylenetriamine 2017


TEACHING EXPERIENCE

**Guest lecturer** in Aquatic Chemistry (EECE 505) for redox chemistry  
Fall 2017

**Guest laboratory assistant** in Environmental Nanochemistry (EECE 534/443)  
Spring 2016

**Teaching Assistant** for  
- Bioprocess Engineering I: Fundamentals & Applications (EECE 506)  
  Spring 2016  
- Properties of Materials (CHE 476)  
  Fall 2013  
- Environmental Organic Chemistry (EECE 448)  
  Spring 2014

**Mentor** for graduate and undergraduate students  
- Ph.D. student: Yaguang Zhu  
  Fall 2016  
- Undergraduate student: Seung Woo Ham  
  Summer 2016  
- Undergraduate student: Gabriella Riek  
  2015-2016

PROFESSIONAL SOCIETY MEMBERSHIPS

Member of American Chemical Society  
2015-present

Member of Geological Society of America  
2016-2017

Member of Clay Mineral Society  
2013-2014

OUTREACH

**Graduate Student Volunteer, “Moving and Shaking” outreach program, WUSTL**  
- Demonstrated global warming and CO₂ sequestration to students in grades 6-8  
  in the St. Louis metro area  
  October in 2013-2017

**Graduate Student Volunteer, Women in Engineering Day, WUSTL**  
- Offered hands-on workshops to female high school students and teacher visitors  
  for the Washington University in St. Louis Chapter of the Society of Women  
  Engineers in Engineering Day  
  February in 2014-2018