

**Permeability and mineral composition evolution of primary seal and reservoir rocks in geologic carbon storage conditions**

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## **Abstract**

It has been reported that deep saline aquifers represent the largest geologic CO<sub>2</sub> storage resource. To better predict containment effectiveness and long-term reservoir behavior of these formations, it is important to understand the potential geochemically-induced changes to the porosity and permeability of both the primary sealing formation and CO<sub>2</sub> storage formation rocks. To investigate these potential changes, an experimental study to probe the geochemical interactions of CO<sub>2</sub>/brine/rock system under geologic CO<sub>2</sub> storage conditions was conducted in a static reaction system. Marine shale (primary sealing formation) and Lower Tuscaloosa sandstone (CO<sub>2</sub> storage formation) core samples taken from the Plant Daniel CO<sub>2</sub> storage test site (Jackson County, Mississippi) were exposed to CO<sub>2</sub> saturated brine in a batch reactor at relevant geologic storage conditions (85°C and 23.8 MPa CO<sub>2</sub> pressure) for six months. X-ray diffraction (XRD), scanning electron microscopy (SEM), computed tomography (CT), and brine chemistry analyses were performed before and after the exposure. Permeability measurements from the Marine shale and sandstone core samples before and after CO<sub>2</sub>/brine exposure indicated a significant effective permeability change. The sealing Marine shale permeability increased following exposure while the permeability of the sandstone from the storage formation was observed to decrease. Analysis results of the primary sealing formation sample (Marine shale) at the Plant Daniel CO<sub>2</sub> storage test site have not been reported before. The permeability decrease of the Lower Tuscaloosa sandstone sample reported in this study verifies the results reported in a previous study. These results have implications for the integrity of the primary seal in a CO<sub>2</sub> storage setting.

***Key words:*** geologic carbon storage; CO<sub>2</sub> sequestration; Marine shale; chemical interaction; permeability; saline aquifer.

## Introduction

Many options have been proposed to reduce or avoid emissions of anthropogenic CO<sub>2</sub> to the atmosphere to ameliorate the impacts of greenhouse gas effects on global climate change. One proposed technology option involves the capture of CO<sub>2</sub> from the gaseous byproduct stream of large point sources (e.g. fossil fuel-fired power plants), compression, and transport of that separated CO<sub>2</sub> in a dense state to sites where it can be injected into deep geologic formations for long-term storage. The Intergovernmental Panel on Climate Change has reported that injection of CO<sub>2</sub> into confined geological formations represents one of the most promising solutions for mitigating global climate change (Pachauri & Reisinger, 2007). Candidate geological formations for possible CO<sub>2</sub> storage include: depleted oil and gas fields, un-mineable coal seams, basalt formations, shale intervals, and deep saline aquifers (Atlas V 2015). Recent studies have been reported regarding the sequestration of CO<sub>2</sub> in geological formations, including a storage capacity estimate for saline aquifers, effects on coal, coupling with enhanced oil recovery, and a modeling study of a CO<sub>2</sub> storage project in a reservoir in Cranfield, Mississippi (Haljasmaa *et al.*, 2011; Rodosta *et al.*, 2011; Delshad *et al.*, 2013; Middleton, 2013; Ranjith *et al.*, 2013; Jia *et al.*, 2016). Deep saline aquifers represent the largest volume class of CO<sub>2</sub> storage targets (Atlas V 2015) due to the large pore volume in sedimentary basins and the high density and solubility of CO<sub>2</sub> at the pressure and temperatures that exist in saline aquifers (Bachu and Adams, 2003). Oil and natural gas-bearing formations are also recognized as having significant CO<sub>2</sub> storage capacity, and CO<sub>2</sub> injection into those formations has the added advantage of enhancing the recoverable hydrocarbons, allowing a field to be more profitable. Demonstration scale injections of CO<sub>2</sub> storage in saline aquifers and hydrocarbon-bearing formations have been performed, and these experiences generate critical information to build confidence in the viability of those options.

The Southeast Regional Carbon Sequestration Partnership (SECARB) has identified the Lower Tuscaloosa formation in the Southeast region of the U.S. as a viable injection horizon for large scale CO<sub>2</sub> storage demonstrations (Rodosta *et al.*, 2011). One SECARB project targeting that formation is a small-scale injection conducted at a coal-fired power plant in Escatawpa called Plant Daniel in Jackson County, Mississippi (Rodosta *et al.*, 2011); another is a larger-scale injection in the Cranfield oil field near Natchez, Mississippi (Rodosta *et al.*, 2011). For both injection locations the storage reservoir is the Lower Tuscaloosa sandstone formation, and the Tuscaloosa Marine shale is the primary confining unit, with the Selma chalk group and Midway shale serving as secondary and tertiary containment units, respectively (SECARB 2016).

The Lower Tuscaloosa sandstone is about 36.5 m thick with an average porosity of 24% and permeability ranging from about 800 to 1,500 mD. The Lower Tuscaloosa sandstone, in southeast Mississippi, is composed of over 90% fine to medium grained sandstone. It is described as white and finely micaceous with a fine clay matrix interbedded with mudstone and siderite nodules (Griffith *et al.*, 2011). The Marine Tuscaloosa shale is a fissile, fine-grained, dark-gray micaceous shale with minor interbeds of calcareous, glauconitic sandstone with some argillaceous limestone lentils, laminated claystone, mudstones, and calcareous siltstone. The Marine Tuscaloosa shale is predominantly composed of quartz, kaolinite, illite, hematite, and siderite based on point-counts of thin-section (Griffith *et al.*, 2011). The average thicknesses of the confining systems are 152, 107, and 396 m for Marine Tuscaloosa shale, Midway shale, and Selma chalk, respectively (Griffith *et al.*, 2011).

As part of the SECARB projects, CO<sub>2</sub> has been injected into the Lower Tuscaloosa sandstone at both sites. About 4,300,000 metric tons of natural and anthropogenic CO<sub>2</sub> have been injected at Cranfield at depths from 2,591 m to 3,124 m, and about 2,490 metric tons of CO<sub>2</sub> have been injected at Plant Daniel at a depth of 2,621 m. As CO<sub>2</sub> is injected into saline aquifers, it will dissolve into the formation fluids, form carbonic acid, lower solution pH, and possibly react with minerals in both CO<sub>2</sub> storage interval and the primary seal above the interval. The acidification sequences will impact the rock's properties (e.g., porosity, permeability, as well as reactive surface area) (Tutolo *et al.*, 2015; Li *et al.*, 2016; Pan *et al.*, 2016). Better understanding how rock/brine/CO<sub>2</sub> interactions affect injectivity and containment effectiveness will build confidence in the successful operation of subsurface CO<sub>2</sub> injection and storage (Delshad *et al.*, 2013).

Investigations into host rock properties using both experimental and modeling studies have been conducted (Luquot & Gouze, 2009; Morse & Arvidson, 2002; Soong *et al.*, 2014b; Zhang *et al.*, 2015). Luquot & Gouze (2009) experimented with flowing CO<sub>2</sub>-enriched aqueous phase through a carbonate core resulting in porosity and permeability changes from dissolution and/or precipitation at *in situ* geologic carbon storage (GCS) conditions of 100 °C and pore fluid pressure of 12 MPa. Specifically, precipitation of Mg-rich calcite resulted in decreased permeability and porosity. Gouze & Luquot (2011) also conducted an X-ray microtomographic characterization of porosity, permeability, and reactive surface changes during the dissolution of pure calcite in a brine/CO<sub>2</sub> mixture and showed that an increase in permeability was due to decreasing the tortuosity for homogenous dissolution. Also, they concluded that extensive GCS in deep saline aquifers that contain carbonate minerals could result in dissolution of these minerals, which could in turn, affect permeability (Gouze & Luquot, 2011). Soong *et al.*, (2014b) found that mineral

dissolution/precipitation could occur under GCS conditions for samples obtained from the Mount Simon formation (Indiana). In addition, Zhang *et al.*, (2015) conducted core-scale numerical simulations of Mount Simon sandstone porosity and permeability evolution under GCS conditions. The simulation predicts dissolution of feldspar and quartz with subsequent formation of kaolinite causing a decrease in permeability. A study conducted by Lu *et al.*, (2012) on CO<sub>2</sub>/rock/brine interaction in the Lower Tuscaloosa formation showed mineral reactions in the Lower Tuscaloosa reservoir were minor during CO<sub>2</sub> injection and brine chemistry remained largely unchanged. The reservoir is composed mainly of minerals with low reactivity (e.g. quartz) which are relatively unaffected by CO<sub>2</sub>. Li *et al.*, (2016) conducted a ten-day batch-reaction study on rock/water/CO<sub>2</sub> interaction at conditions relevant to GCS (T = 100 °C, P = 10 MPa) with rock obtained from the Guantao formation of Bohai Bay Basin, China. The major mineral composition of the rock is quartz balanced with K-feldspar, albite and clay minerals. They reported K-feldspar and albite dissolution as well as the formation of kaolinite, chlorite and Fe-bearing minerals of pyrite and hematite post reaction. In addition, HCO<sub>3</sub>, Ca, Mg and K and trace elements of Al, Cr, Mn, Ni and Zn in water showed a significant increase post reaction. Tutolo *et al.*, (2015) conducted studies in K-feldspar rich sandstone from the Eau Claire formation (Indiana) under GCS conditions (150 °C, and 20 MPa) using a flow-through apparatus. The results indicated dissolution of feldspar and precipitation of secondary aluminum minerals, such as boehmite. They also reported the decrease in bulk permeability and lower porosity in the post-experiment core samples.

Though laboratory studies have been conducted to investigate the interaction between CO<sub>2</sub> and the minerals comprising the storage interval rocks, few studies have been conducted to investigate the interaction between CO<sub>2</sub> and the minerals comprising the rock of the primary seal above the CO<sub>2</sub>

storage interval (Mouzakis et al., 2016; Miller et al., 2016). In fact, dissolution of carbonates and silicates in the primary seal is possible when the seal is in contact with CO<sub>2</sub>-saturated brine (Miller et al., 2016). The rate of dissolution is dependent on pH decreases in the brine from CO<sub>2</sub> dissolution, reactive area/mass transfer properties, rock/water ratio, and rock composition (Morse & Arvidson, 2002; Luquot & Gouze, 2009; Xiao *et al.*, 2017a). Dissolution of carbonates and silicates can result in changes in permeability, porosity, and reactive surface area. Cation concentration increases can supersaturate pore fluids with carbonates, with subsequent precipitation that can further alter porosity and permeability of the primary seal.

To fill this knowledge gap, the present study considers the effects of GCS on a sample from the primary confining unit above the Lower Tuscaloosa sandstone CO<sub>2</sub> storage interval (Marine shale) through laboratory experiments exposing the sample to CO<sub>2</sub>-saturated brine for six months at *in situ* conditions. Mineralogical, textural, and geochemical changes as a result of the exposure were determined using X-ray diffraction (XRD), computed tomography (CT) scanning, optical microscopy, scanning electron microscopy (SEM), and brine chemistry analyses. A Lower Tuscaloosa sandstone sample was also exposed to CO<sub>2</sub>-saturated brine for six months and analyzed by XRD, CT, SEM, etc. to verify property changes of another sample taken from the same interval reported in Soong et al. (2016).

## **Experimental**

### **Core Samples and Brine**

Two core samples from the Plant Daniel test site, approximately 2.54 cm in diameter by 5.08 cm in length, were used in this study. One was a Marine shale core from a depth of 2,418 m and the other was a Lower Tuscaloosa sandstone core from a depth of 2,611 m. Marine shale is the primary seal of Lower Tuscaloosa sandstone, which serves as the CO<sub>2</sub> storage reservoir. The approximate major mineral compositions of the Lower Tuscaloosa sandstone sample and the Marine shale sample were determined by semi-quantitative bulk XRD analysis (Table 1). The chemical composition of the synthetic brine (Table 2) was designed based on the fluid chemistry of Lower Tuscaloosa brine. The initial pH of the synthetic brine was 5.4. Since the Lower Tuscaloosa brine is in contact with rocks in Lower Tuscaloosa formation for very long time so the equilibrium condition is expected to have been reached. Therefore, no reactions are expected to take place between the synthetic brine and rock samples before CO<sub>2</sub> is added. Before any measurements, the samples spent at least three days in a nitrogen-purged desiccator at relative humidity of 8-10%.

### **Reactors and Experimental Procedures**

A set of 1.8 liter (N4683-T-HC-7500 C276) high-pressure vessels (9.53 cm I.D. by 26.67 cm depth) manufactured by Parr Instrument Company, Erie, PA, were used for this study. An open Teflon cell (7.62 cm I.D. × 10.16 cm length) and a smaller Teflon reaction cell (6.35 cm I.D. × 9.52 cm length) were used inside the pressure vessel. An ISCO 260D syringe pump was used to charge each vessel with CO<sub>2</sub> and to maintain the pressure in the reactor. Temperature was maintained and controlled within ±1°C. A sketch of the reaction system can be found in Figure 1.

The standard procedure for conducting the experiments was as follows:

1. The Teflon container holding the samples (core and two small chips) and brine was loaded into another large Teflon container in the pressure vessel.
2. The gap between the sample-holding container and the large container was filled with brine, insuring the CO<sub>2</sub> phase remains saturated with water vapor without substantially altering the salt concentration in the sample-holding container.
3. The pressure vessel was closed and purged with CO<sub>2</sub> three times to remove air.
4. The pressure vessel was charged with CO<sub>2</sub> to 4.08 MPa and heated to 85°C.
5. CO<sub>2</sub> was added to a pressure of 23.8 MPa and held at these conditions for 6 months.
6. Upon termination of the experiment the temperature and pressure were slowly returned to ambient, and the samples were removed.
7. The solid samples were rinsed with deionized water multiple times to remove residual NaCl and dried in a desiccator under N<sub>2</sub> flow.
8. Liquid from the sample-bearing container was recovered for analysis. The reacted brine analysis is given in Table 2.

### **Measurements and Analysis methods**

Prior to and after the six-month test, the solids were analyzed by CT scanning, XRD, SEM, and optical reflected light microscopy. Inductively coupled plasma - optical emission spectroscopy (ICP-OES) was used to determine metal concentrations in the liquid samples, but due to high salt concentrations, sample dilution with distilled/deionized water was required. Solutions were analyzed for the full range of metals quantifiable by ICP-OES including Al, Si, and Fe. The details

of cation and anion analyses, x-ray diffraction, and scanning electron microscopy-energy dispersive x-ray analyses were reported elsewhere (Soong *et al.*, 2014a).

Porosity and permeability of the samples were measured both before and after the exposure. The porosity was measured using a helium porosimeter (HP-401, TEMCO, Inc., Tulsa, OK) at 0.7 MPa at ambient temperature. For the high-permeability sample (sandstone), a TEMCO Ultraperm 500 "flow-through" permeameter was used. The low-medium permeability core (Marine shale) was measured using the pressure transient method (details of the method were reported in Siriwardane *et al.*, 2009). The permeability of the core samples measured at the confining pressure close to the depth of the core was collected and with various effective pressures to obtain the permeability profile of the core. The initial porosities were 26.5% for the sandstone core and 8.65% for the Marine shale core. The initial permeability was 2955 mD for the sandstone core and 47  $\mu$ D for the Marine shale core.

All the cores were scanned in the North Star Imaging M-5000 industrial CT scanner. Each of the reconstructed pre and postimages of the 2.54 cm-diameter Lower Tuscaloosa sandstone core each has a voxel resolution between 21 and 22  $\mu$ m. The Marine shale pre-exposure core was scanned at a resolution of 32.7  $\mu$ m and the post-exposure core was scanned at 21.2  $\mu$ m. All resolutions mentioned are not fine enough to resolve the micro- to nano-scale porosity present in a sandstone or shale rock. The undetectable pores may connect larger voids that facilitate mass transport. Instrument settings, operating conditions, parameters are described elsewhere (Soong *et al.* 2016). The reconstruction properties of the images were selected to provide the highest fidelity rendition of the scanned sample and to construct a 3-D volumetric representation of the object. The data

were exported as a series of 16-bit grayscale cross-sectional TIFF images of the core. Image post processing was performed using the open-source software ImageJ (Rasband 2014) and PerGeos<sup>®</sup>.

## **Results and discussion**

### **Exposure Response of the Storage Formation Rock (Lower Tuscaloosa sandstone)**

Figure 2 shows the permeability of the Lower Tuscaloosa sandstone measured as a function of the effective pressure. The post-exposure permeability of 2,400 mD was about 17% lower than the measured pre-reaction permeability of 2,900 mD in the fresh core at the effective pressure of 35.7 MPa. This result suggests that the CO<sub>2</sub>/brine exposure alters the pore characteristics by restricting flow and resulting in permeability reductions, and this result is consistent with permeability reduction of another Lower Tuscaloosa core after 6-month exposure to CO<sub>2</sub> saturated brine, as reported in Soong et al. (2016). The initial porosity of the Lower Tuscaloosa sandstone was 26.5%, and the post-reaction porosity of the rinsed and dried Lower Tuscaloosa sample was 24.8%, which shows alteration of pore characteristics.

Figure 3 shows CT analysis results of the sandstone before and after the six-month exposure to the CO<sub>2</sub>/brine environment. The pre-exposure scans (Figure 3A) of the sandstone core were scanned at a 21.2 micron resolution, and the post-exposure core was scanned with a resolution of 21.8 microns (Figure 3B). The pre- and post-exposure scans are similar in location for each image pair. Both pore space (dark zones) and higher attenuating minerals within the core (bright zones) can be observed in Figures 3A and 3B. Figure 3C (pre-exposure) and 3D (post-exposure) are zoomed-in images from the red square highlighted regions presented in the lower left portion of Figures 3A and 3B. The yellow circled region in Figure 3C shows a gray void structure present in the pre-exposure scan that is no longer visible in the post-exposure scan Figure 3D. Moreover, higher attenuating minerals (bright spots on Figure 3C) appear to have been altered after six month of exposure to CO<sub>2</sub>/brine (Figure 3D). This level of detail was only discernable in the zoomed-in

images. The void was located approximately 2 mm from the cores edge and may indicate that mineral precipitation closed the void after the core was exposed to CO<sub>2</sub> saturated brine.

To ensure the observed precipitation was not a result of slight changes in resolution or an error in 2D slice matching from pre to post-exposure, the cropped 2D stacks that included the slices presented in Figures 3C and 3D were examined in 3D using PerGeos® (Figures 4A and 4B). The red 3D pore space disappears from pre-exposure (Figure 4A) to post-exposure (Figure 4B) further confirming the pore space closed after six months brine/CO<sub>2</sub> exposure. The resolutions of these two scans are not fine enough to resolve the micro-porosity present in a sandstone core. Micro-porosity is known to connect larger scale voids and contribute to flow. However, the observed precipitation occurred within a pore approximately ~200 µm in diameter, well above the resolution detectable within the scans reviewed. Undetectable micro-porosity may have influenced the observed reductions in porosity and permeability. However, the pores detectable at this resolution would contribute more to mass transport and, therefore, would contribute more to a reduction in mass transport if closed.

Based on this evidence it is theorized that the observed 17% permeability decrease and 6.4% porosity decrease result from mineral precipitation occurring in the sample pores with a net effect of restricting flow. Mineral precipitation may also have occurred within pore-throats in the porous medium, thus contributing to net permeability decreases, as illustrated in these CT scans. Studies of acidizing hydrocarbon reservoirs for enhanced oil recovery such as Smith *et al.*, (2013) have identified similar permeability decreases as well as a similar study conducted with CO<sub>2</sub>/brine/Mount Simon sandstone (Soong *et al.*, 2014b).

Comparing the analyses of the post reacted brine composition with that of the fresh brine (Table 2) showed that after the six month exposure period, the concentrations of Al, Fe, Mg, Na, and Si had increased. This change in solution chemistry suggested that CO<sub>2</sub>-acidized brine dissolved some of the non-quartz minerals.

Figure 5A-F shows selected secondary electron SEM images of the Lower Tuscaloosa sandstone sample. The specific site selected is a feldspar grain (identified based on EDS) which is expected to be more susceptible to chemical change during exposure. The fresh sample is shown in Figure 5A and 5D. Figure 5B and 5E show the sample images after six months of CO<sub>2</sub>/brine exposure. Figure 5C and 5F further illustrate the sample after additional rinsing with deionized water to remove the NaCl deposited on the surface. The NaCl surface deposit was probably formed due to slow diffusion of residual brine out of pore structure to the surface during drying, which is commonly referred to as a “salting out” effect. In the top center of the fresh (Figure 5D) and exposed (Figure 5F) circled images, possible evidence of mineral dissolution was observed. Possible mineral dissolution and precipitation were also observed after the six-month CO<sub>2</sub>/brine exposure (by comparing middle and bottom circled areas in Figure 5D (fresh) to those circled areas in Figure 5F (exposed)). The precipitation of secondary minerals (possibly amorphous SiO<sub>2</sub> (am) and kaolinite, as reported in Zhang et al., in press) is possibly the primary contributor to a decrease in bulk permeability. When CO<sub>2</sub> is injected into a saline formation, the brine in the reservoir becomes more acidic. The increase in acidity can lead to some dissolution of minor minerals in the sandstone such as feldspar and chlorite that are stable in the original conditions (Fu *et al.*, 2009; Zhang *et al.*, 2016). The increase in cation concentration produced by mineral dissolution can

supersaturate the pore solution with respect to other minerals resulting in precipitation of secondary minerals like SiO<sub>2</sub> (am) and kaolinite. Zheng *et al.*, (2015) conducted an experimental investigation of quartz-feldspar-detrital sandstone properties under CO<sub>2</sub>/NaCl solution/rock interaction. Their results show that the addition of CO<sub>2</sub> enhanced the partial mineral dissolution and the compressibility for sandstone, and a permeability reduction is observed. The injected CO<sub>2</sub> could be dissolved in pore fluid and precipitated with the calcium, magnesium, and ferrous ions in pore solution from the sandstone skeleton thus resulted in the permeability reduction (Zheng *et al.*, 2015).

#### **Exposure Response of the Primary Sealing Formation Rock (Marine shale)**

The characterization of the Marine shale sample was done using the same procedure described for the Lower Tuscaloosa sandstone sample. The permeability that was measured at *in situ* conditions corresponded to a depth of ~ 2,418 m (effective pressure of 33.5 MPa). The Autolab unit (NER, Inc., White River Junction, VT) with argon was used for more precise measurements of the Marine shale permeability for both fresh and exposed samples due to the low permeability of the shale. Figure 6 shows the permeability as a function of different effective pressures. Here, a significant increase in permeability (170 μD of the core when exposed for six months vs. 30 μD of the fresh core at the effective pressure of 33.5 MPa) was observed. Mineral dissolution could increase the average size of pathways which could lead to increased permeability. The porosity of the fresh sample was 8.65%, and the porosity measured after the six month CO<sub>2</sub>/brine exposure was only slightly lower at 8.56%.

CT analysis results of the Marine shale core before and after the six-month exposure to the CO<sub>2</sub>/brine environment are shown in Figure 7. Figure 7 displays approximately the same slice from pre- (7A) and post- (7B) exposure. One main fracture spanning the diameter of the core in Figure 7A appeared to have decreased in size after six month exposure in CO<sub>2</sub>/brine environment (Figure 7B). On the other hand, two adjacent fractures were widened in the post-exposure image (Figure 7B). Furthermore, dense materials (bright spots) were formed within the left-most fracture following exposure to CO<sub>2</sub> saturated brine (Figure 7B circled areas).

Figure 8 contains resliced images in the YZ-plane for pre- (8A) and post-exposure (8B) samples. Two regions of interest (ROI) are identified: a red rectangle and an orange oval. The red rectangle focuses on a fracture that became more connected after six month exposure. A widened and more connected fracture detectable at the scan resolution would contribute to mass fluid transport. Additionally, the orange oval highlights a fracture where some dense mineral growth is apparent after the six month exposure (Figure 8A to 8B). The combination of both may result in the increase of the permeability of the sample after the six month exposure. Precipitation caused the main fracture to close in diameter while two large fractures widened over the six-month exposure. The additional stresses within the precipitated fracture may have caused the adjacent fractures to expand.

Both fracture connection and mineral precipitation in the fracture after the CO<sub>2</sub>/brine exposure are indicated by CT images, and permeability results show that the combination of both causes an increase of permeability of the sample after the six month exposure (Figure 6). To better interpret those results, the nature of these fractures, their relevance to *in situ* behavior of formation rock, and implications for GCS system performance need to be considered. The evolution of fracture

features in the Marine shale cores may be related to a geochemical alteration of the sample along a bedding plane due to a preferential geochemical alteration related to compositional differences (e.g., presence of more easily weathered mineral(s) along specific planes). It may also be due to delamination of the sample along the bedding plane after the sample was removed from the *in situ* confining stress. This decompression and mechanical delamination would be augmented by sample swelling with exposure to brine. A modified experimental approach would need to be pursued to resolve the extent to which each of these factors contributed to fracture evolution in the Marine shale core sample under experimental conditions. Also, because the direction of observed shale fracturing/delamination is parallel to the bedding plane, and nominally orthogonal to the path of leakage through the seal, the change in effective permeability in the X-Y plane associated with shale delamination that could potentially occur in the Marine shale, would not significantly contribute to the change in effective permeability of the seal in the Z direction. A large permeability increase in the Z direction due to delamination cracks would depend somewhat on the degree of interconnection of the cracks. As such, the overall impact to containment effectiveness of the Marine shale seal may be negligible in the Lower Tuscaloosa GCS system. Further experimental simulation and modeling is warranted to further explore this idea.

The post-reaction brine was analyzed following contact with the Marine shale and CO<sub>2</sub> (Table 2). Comparing the reacted brine with the fresh brine, the following trends were observed. The concentration of Ca, Fe, Mg, Na, and Si increased after the six-month exposure period. Except for K, the increases in reacted brine concentration for the Marine shale were more than those observed for the Lower Tuscaloosa sandstone core exposure experiment. This observation was not surprising since the shale contains a higher content of minerals (i.e., chlorite, plagioclase, etc.) that

are more susceptible to CO<sub>2</sub>/brine attack. Only a slight increase in the concentration of Ca was observed even though 5% of the Marine shale is calcite. Preferred dissolution of silicates like chlorite and plagioclase over calcite is possibly the reason for slow increase of Ca in solution.

The chemical reactions between reservoir rock and fluids involve two types of minerals: the first type are the relatively fast-reacting minerals including Ca, Mg, or Fe-rich frame work minerals such as feldspars, clays, micas, and the second type includes minerals like Fe oxides and quartz which interact slowly with CO<sub>2</sub> (Zheng *et al.*, 2015). The addition of CO<sub>2</sub> induced the dissolution of feldspathic minerals, which increased the concentration of metal ions such as K and Na and may decrease the concentration of calcium ions which are precipitated by carbonic acid. Dissolution of feldspar and other silicates can also lead to super-saturation of SiO<sub>2</sub> and precipitation of SiO<sub>2</sub> (Miller *et al.*, 2016). In the NaCl/CO<sub>2</sub>/rock environment, the feldspar reacts with water and generates mica, kaolinite, etc. while the dissolved CO<sub>2</sub> can result in formation of carbonate minerals such as the dolomite, calcite, siderite, etc. (Zheng *et al.*, 2015). Studies of CO<sub>2</sub> injection into depleted oil and gas reservoirs have shown that the initial chemical equilibrium between the saline formation fluid and reservoir rock may be disturbed resulting in new chemical reactions (Fischer *et al.*, 2010). Such interactions can result in changes in the physical and chemical properties of the reservoir system (Wigand *et al.*, 2008; Fischer *et al.*, 2010; Soong *et al.*, 2014b; Zhang *et al.*, 2015). The Marine shale located above the potential storage formation (Lower Tuscaloosa sandstone) is considered as the primary seal. The observed increase in permeability after the CO<sub>2</sub>/brine exposure from this study is likely due to the heterogeneity of the core sample and the experimental setup which resulted in core sample cracking during the exposure period. Those results may not represent actual *in situ* behavior. It also can be seen from Table 1 that the

major mineral composition is not significantly different between sandstone and Marine shale. In addition, the Marine shale does have more reactive feldspar and calcite than the sandstone. Dissolution of the reactive K-feldspar and calcite could have created additional connective pathways thus contributing to an increase in permeability after the CO<sub>2</sub>/brine exposure. This might impact the integrity of the long-term storage of CO<sub>2</sub>. However, the very low permeability of the shale relative to the sandstone and the capillary pressure barrier effect would suppress CO<sub>2</sub> to enter the pore space of the caprock, which limits bulk rock dissolution and reduces the risk to the seal rock formation (Tian *et al.*, 2014; Xiao *et al.*, 2017b). Furthermore, the secondary cap rock formation, the Selma chalk, above the Marine shale was found not to be reactive with CO<sub>2</sub>/brine in our previous study (Soong *et al.*, 2016). In summary, while potential geochemical alteration of sealing intervals in GCS scenarios could significantly affect local seal behavior, the presence of a relatively thick primary caprock, and secondary low permeability sealing intervals will likely minimize upward CO<sub>2</sub> and brine migration. To be specific, even though the primary confining layer to the Lower Tuscaloosa formation (the Marine shale) shows some evidence of reactivity and fracturing in experimental studies, the presence of the Selma chalk as a secondary containment unit gives confidence that effective containment will be ensured.

For the Lower Tuscaloosa sandstone sample, the combined information from XRD, SEM, CT scanning, and brine analysis indicate dissolution of minerals, most likely feldspar, kaolinite, and chlorite in flow pathways along with precipitation of minerals in flow pathways of the Lower Tuscaloosa sandstone sample. For the sandstone sample, mineral dissolution, most likely feldspar, and secondary mineral precipitation in flow pathways had the net effect on decreasing permeability. These results suggest that the injection of CO<sub>2</sub> into a deep saline aquifer can affect porosity as a

result of both mineral dissolution and precipitation in the formation. The change of porosity due to mineral reactions can adversely influence the permeability. This permeability change depends not only on the porosity, but also on the details of the pore space geometry and the distribution of precipitates within the pore space.

In future work, there will be two focuses: 1) determine if the permeability increase of the Marine shale sample results in an impact to containment effectiveness of the Marine shale seal in the Lower Tuscaloosa GCS system; 2) use multiple Marine shale samples from different depths to verify the results reported in this study. To address the first, a reservoir-scale model will be developed to investigate how thick the zone will be that has a permeability increase in the Marine shale. To address the second, multiple Marine shale samples will be obtained from the Plant Daniel CO<sub>2</sub> storage site to conduct duplicate experiments.

## Conclusions

In this study, chemical interactions between a primary seal sample (Marine shale core sample) and CO<sub>2</sub>-saturated brine was investigated under *in-situ* GCS conditions, as well as a CO<sub>2</sub> storage reservoir sample (Lower Tuscaloosa sandstone core sample). The Lower Tuscaloosa CO<sub>2</sub> storage reservoir was immediately below Marine shale primary seal. The interaction between core samples and CO<sub>2</sub>-saturated brine was investigated using a six-month duration static system. CT, XRD, SEM, petrography, brine composition, porosity, and permeability analyses were performed on the samples before and after the exposure to CO<sub>2</sub> saturated brine under GCS conditions. For the Marine shale, the significant change in permeability is due to the combined effects of reactive mineral composition, sample heterogeneity and sample delamination, though the permeability of the altered shale was observed to be 1,000 times less than the permeability of the sandstone. Moreover, after the Marine shale sample was retrieved from deep depth below the surface, the drop in confining pressure might lead to formation of secondary fractures due to decompression and subsequent delamination. The formation of these secondary fractures could lead to over-prediction of the permeability increase. For the Lower Tuscaloosa sandstone, there was a 6.4% decrease in porosity and a 17% decrease in permeability found in the sandstone core after it was exposed to CO<sub>2</sub> saturated brine for six months. The decrease in porosity and permeability was due to feldspar dissolution, migration and secondary mineral precipitation altering the sandstone pore/crack structure. The low content of active mineral phases in the Lower Tuscaloosa sandstone sample and the high initial porosity of the sample lead to a smaller permeability change for the sample after the exposure. Our previous study suggests that even with an increase in the Marine shale permeability, the existence of the secondary and tertiary seals are likely to provide a stable cap rock seal in the presence of CO<sub>2</sub>.

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## **Disclaimer**

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## **Author Disclosure Statement**

The authors declare that no competing financial interests exist.

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## List of Figures

**FIG. 1:** Sketch of rock—brine—CO<sub>2</sub> reaction system. The sample to brine volumetric ratio in Teflon cell #1 is 1 : 5.

**FIG. 2:** The permeability of Lower Tuscaloosa sandstone as a function of the effective pressure.

**FIG. 3:** Lower Tuscaloosa A) Pre-exposure Slice and B) Post-exposure Slice each with the identical square region of interest (ROI) highlighted in red. C) Cropped Pre-exposure and D) Cropped post-exposure zoomed-in images of A and B located approximately 2 mm from the edge of core. The yellow circle highlights the pore space change from exposure.

**FIG. 4:** Lower Tuscaloosa sandstone A) Pre-exposure, B) Post-exposure red pores (in red) and purple dense materials. The yellow circle highlights the region where precipitation occurred from A to B. Cropped region located approximately 2mm from the edge of core.

**FIG. 5:** The SEM images of the Lower Tuscaloosa sandstone fresh (5A, 5D) vs. exposed (5B, 5E) to CO<sub>2</sub>/brine for six months. Figure 5C and 5F are images of 5B and 5C rinsed with DI water to remove residual NaCl.

**FIG. 6:** The permeability of Marine shale as a function of effective pressure.

**FIG. 7:** A) Marine Shale pre-exposure slice and B) Marine Shale post-exposure slice. Aperture changes of fractures are indicated and precipitated dense materials are marked in red circles.

**FIG. 8:** Marine shale re-sliced images in the YZ-plane A) Pre-exposure and B) Post-exposure. Two ROIs are highlighted one red rectangle showing dissolution and one orange oval showing precipitation.

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Table 1. XRD analysis of the Lower Tuscaloosa sandstone and the Marine shale. (Analysis was performed by Weatherford Laboratories.)

Table 2. The analysis of synthetic brine and the brine interacted with CO<sub>2</sub>/sandstone for six months under CO<sub>2</sub> sequestration conditions.

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