Experimental Study of Porosity Changes in Shale Caprocks Exposed to Carbon Dioxide-Saturated Brine II: Insights from Aqueous Geochemistry

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Received: December 24, 2015

Accepted in revised form: May 22, 2016

Abstract

Laboratory experiments evaluated two shale caprock formations, the Gothic Shale and Marine Tuscaloosa Formation, at conditions relevant to carbon dioxide (CO₂) sequestration. Both rocks were exposed to CO₂-saturated brines at 160°C and 15 MPa for ~45 days. Baseline experiments for both rocks were pressurized with argon to 15 MPa for ~35 days. Varying concentrations of iron, aqueous silica, sulfate, and initial pH decreases coincide with enhanced carbonate and silicate dissolution due to reaction between CO₂-saturated brine and shale. Saturation indices were calculated and activity diagrams were constructed to gain insights into sulfate, silicate, and carbonate mineral stabilities. Upon exposure to CO₂-saturated brines, the Marine Tuscaloosa Formation appeared to be more reactive than the Gothic Shale. Evolution of aqueous geochemistry in the experiments is consistent with mineral precipitation and dissolution reactions that affect porosity. This study highlights the importance of tracking fluid chemistry to clarify downhole physicochemical responses to CO₂ injection and subsequent changes in sealing capacity in CO₂ storage and utilization projects.

Keywords: CO₂ capture and storage; geochemical reactions; global-scale and regional-scale environmental impacts; inorganic geochemistry; thermodynamics and equilibrium

Introduction

GEOLOGIC CARBON CAPTURE utilization and storage (CCUS) is a promising approach for managing anthropogenic carbon dioxide (CO₂) emissions. Successful deployment of CCUS technologies relies on the presence of impermeable caprocks to facilitate structural trapping of injected CO₂. Suitable caprocks include shales, whose fine-grained, clay-rich nature make them excellent barriers to gas

and fluid migration. Understanding how brine-CO₂-rock reactions may alter shales is not only vital for predicting the long-term effectiveness of containment, but also provides insight into hydrocarbon extraction activities in which shale formations are produced as unconventional reservoir rocks. Economically favorable CCUS options often include a carbon utilization component, such as CO₂-enhanced shale gas recovery (EGR) (Schaefer *et al.*, 2014). Utilization of supercritical CO₂ as a “foam” hydraulic fracturing fluid component for tight (low permeability) oil and gas formations is also receiving increased attention as an alternative to the typical approach in which acidic aqueous fluids are used (Palmer and Sito, 2013; Barati and Liang, 2014).

Laboratory experiments provide valuable insight into geochemical and mineralogic changes induced by interactions among shale, brine, and CO₂ (e.g., Kaszuba *et al.*, 2003, 2005; Kohler *et al.*, 2009; Alemu *et al.*, 2011). Other experimental studies have addressed additional specific aspects of shale-brine-CO₂ interactions of potential CCUS caprocks,

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the Gothic Shale and Marine Tuscaloosa Formation. Karalidis *et al.* (2013) and Marcon and Kaszuba (2015) evaluated the potential for metal mobilization from the Marine Tuscaloosa Formation and from the contact of the Gothic Shale with an underlying carbonate reservoir, respectively, under conditions relevant to CCUS. Jung *et al.* (2013) and Zhong *et al.* (2014) examined the potential for organic and metal mobilization from the Gothic Shale in response to CO₂ injection. In Part I of this two-part study, Mouzakis *et al.* (2016) investigated the impacts of geochemical reactions on nano- and micron-size porosity development under experimental conditions relevant to CCUS. Neutron scattering, electron microscopy, and other pore network characterization techniques were used to examine nanoscale changes on mineralogic aspects of porosity, pore connectivity, pore size distribution, and internal surface area of both the Gothic Shale and the Marine Tuscaloosa Formation. Changes to these pore network characteristics can significantly affect fluid saturation distribution, hydraulic conductivity, and wettability of caprock and reservoir rock which, in turn, may impact fluid containment and hydrocarbon production, respectively (Kaveh *et al.*, 2014; Yao *et al.*, 2014; Sarmadivaleh *et al.*, 2015; Arif *et al.*, 2016).

In this work, which is a continuation of the Mouzakis *et al.* (2016) study, we evaluate how aspects of the aqueous geochemistry of these same experiments evolve over the duration of the experiments. This information is synergistic with the mineralogic data determined in Part I of this study and constrains how porosity and pore connectivity, and ultimately geofluid storage and production, may change with time as a result of coupled physicochemical processes. As Song and Zhang (2013) highlight, understanding geochemically induced changes to pore networks is vital to accurately predicting the long-term behavior of caprock formations.

Experimental Protocols

Batch experiments

Samples of Gothic Shale or Marine Shale of the Tuscaloosa Group (henceforth referred to as the Marine Tuscaloosa) were reacted with formation specific brine and supercritical CO₂ in hydrothermal experiments at 15 MPa and 160°C as described by Mouzakis *et al.* (2016). Two control experiments were also conducted (in which argon was used to pressurize the reactors in lieu of CO₂) to establish a baseline understanding of brine-rock interactions and provide a basis for evaluating CO₂-brine-rock interactions. In this article, the brine-reacted experiments are referred to as Gothic-Brine and Marine-Brine, and the CO₂-reacted experiments are referred to as Gothic-CO₂ and Marine-CO₂. The rocks are described in detail by Mouzakis *et al.* (2016) and Heath *et al.* (2011).

Analytical methods

Brine samples were periodically sampled and analyzed during the experiments. Extracted brine samples cooled and depressurized to ambient conditions within a few seconds and were subsequently processed. Retrograde reactions with minerals that may occur during a prolonged quench process were consequently avoided and solution composition was analyzed along a reaction pathway. Fluid samples were fil-

tered using a Millipore 0.45 μ m filter. To prevent mineral precipitation, the samples for cation analysis were acidified to pH 2 using trace metal grade nitric acid. Mineral precipitates were not observed in any of the brine samples. Major cation, anion, and minor constituent concentrations in the aqueous samples were determined by inductively coupled plasma optical emission spectroscopy, ion chromatography, and inductively coupled plasma mass spectrometry, respectively. Additionally, pH and total dissolved inorganic carbon were measured at “bench” conditions (degassed samples at 25°C and 0.1 MPa) using a carbon coulometer according to the methods of Chopping and Kaszuba (2012). *In situ* values of total dissolved inorganic carbon were determined by analyzing a sample of brine collected in a glass gas-tight syringe.

Upon termination, or “quench,” the heated, insulating pressure vessel jackets were removed to quickly cool the experiments to minimize retrograde reactions of the fluids and rocks. After terminating each experiment, the remaining brine was filtered using a Millipore 0.45 μ m filter and analyzed according to the same protocols used for the other aqueous samples. The geochemistry of the quench sample and the aqueous sample collected immediately before the quench were compared to determine retrograde reactions that may have occurred while cooling and degassing the experiments.

Geochemical models and calculations

Geochemical calculations were performed to determine *in situ* pH, aqueous species activities, and the saturation state of the brine with respect to different minerals. We used Geochemist's Workbench 10.0 (GWB), the b-dot ion association model, and the resident thermo.tdat database (Bethke and Yeakel, 2014) according to published methods (Chopping and Kaszuba, 2012; Lo Ré *et al.*, 2014; Marcon and Kaszuba, 2015). We used thermo.tdat because it is internally consistent and handles aluminum speciation more adeptly than other available databases (Kaszuba *et al.*, 2011). The ion size parameter for CO₂(aq) in this database was changed to -0.5 to correctly simulate the salting-out behavior of CO₂ (Allen *et al.*, 2005). Initial oxygen values were assumed to be negligible due to sparging of the brine (Mouzakis *et al.*, 2016).

The pH at *in situ* pressure and temperature conditions was calculated for samples collected from the brine-reacted baseline experiments by speciating the fluid at 160°C using bench pH, total dissolved inorganic carbon measured at the bench and at *in situ* conditions, and the aqueous geochemical data (Table 1). *In situ* pH was calculated for CO₂-reacted experiments using the method of Newell *et al.* (2008) and total dissolved inorganic carbon calculated for *in situ* conditions using the equation-of-state of Duan *et al.* (2006). Hereafter, unless otherwise specified, *in situ* pH will be simply referred to as pH. Total dissolved inorganic carbon was measured for samples withdrawn from the CO₂-reacted experiments, but the results were inconsistent due to analytical difficulties and were therefore not used in the pH calculations. We were able to justifiably substitute equation-of-state values for measured values because the brine was saturated with CO₂ for the duration of the experiments.

Results and Discussion

Aqueous geochemical data from the four experiments are presented in Table 1 and selected data are shown in Figs. 1–5.

TABLE 1. AQUEOUS GEOCHEMISTRY FOR FOUR SHALE+BRINE±CO₂ EXPERIMENTS

Time (h)	Na	K	Ca	Mg	Fe	SiO ₂ (aq)	Cl	SO ₄	ΣCO ₂ (bench)	ΣCO ₂ (in situ)	pH (bench)	pH (in situ) ^a	Charge balance
Water chemistry (mmol/kg), brine-reacted Marine Tuscaloosa experiments (Marine-Brine), 160°C, 15 MPa													
Initial Brine ^b	2,799.3	67.8	324.5	6.0	DL	0.76	3,341.7	2.5	0.3	na	7.1	6.5	2.6%
24	2,429.1	64.2	279.6	5.8	DL	0.75	3,406.8	2.8	0.3	0.4	5.7	5.8	-5.4%
187	2,721.4	73.0	336.2	6.5	0.62	1.20	3,491.1	2.8	0.2	1.0	5.5	5.2	-0.2%
354	2,532.7	64.0	300.1	6.0	0.36	1.24	3,441.6	2.4	0.06 ^c	1.2	5.4	4.9 ^c	-3.6%
576	2,708.3	67.2	326.2	6.6	0.11	1.32	3,692.9	2.2	0.2	0.9	5.6	5.3	-3.6%
698	2,603.0	56.3	271.7	5.6	DL	1.15	3,590.0	2.3	0.2	1.0	5.9	5.3	-5.6%
861	2,585.2	66.9	320.1	6.5	0.45	1.42	3,631.1	2.3	0.2	1.0	5.5	5.2	-4.7%
Quench ^d at 864	2,517.6	60.8	315.2	6.3	DL	1.27	3,690.0	2.3	0.2	na	5.6	na	-6.8%
Uncertainty	±34	±5.2	±5.1	±0.3	±0.02	±0.05	±50	±0.1	±6%	na	±0.1	±0.1	na
Water chemistry (mmol/kg), supercritical CO ₂ and brine-reacted Marine Tuscaloosa experiments (Marine-CO ₂), 160°C, 15 MPa													
Initial Brine ^b	2,942.1	75.4	336.1	7.1	DL	0.81	3,865.2	2.6	0.1	na	7.2	5.5	-2.2%
27	2,701.8	45.3	332.6	6.8	0.11	1.61	3,790.1	3.0	7.2	^e	5.0	3.6	-5.1%
122	2,705.0	68.9	335.6	7.1	0.17	1.85	3,834.8	2.5	7.8	^e	4.9	3.6	-5.2%
305	2,400.0	61.6	276.6	6.2	0.41	1.73	2,767.0	1.9	9.3	^e	5.0	3.7	4.4%
481	2,646.3	63.9	314.2	6.7	0.39	2.00	3,410.8	1.9	10.7 ^f	^e	5.1	3.8	-0.9%
694	2,531.9	71.2	333.0	7.3	0.65	2.10	3,607.3	1.6	12.2	^e	5.0	3.8	-4.7%
1,006	2,528.1	67.7	333.5	7.2	0.82	1.80	3,604.8	1.8	0.8	^e	5.2	3.4	-4.8%
Quench ^d at 1,009	2,552.7	65.4	326.1	7.2	0.80	1.60	3,586.7	2.0	14.5	na	5.1	na	-4.4%
Uncertainty	±34	±5.2	±5.1	±0.3	±0.02	±0.05	±50	±0.1	±6%	na	±0.1	±0.1	na
Water chemistry (mmol/kg), brine-reacted Gothic shale experiments (Gothic-Brine), 160°C, 15 MPa													
Initial Brine ^b	191.1	4.0	1,354.5	29.8	DL	DL	2,901.9	0.1	0	n/a	6.8	5.0	1.1%
26	161.7	DL	1,135.3	26.8	DL	1.78	2,932.6	0.8	0.2	0.4	6.0	5.4	-8.3%
143	259.6	6.1	1,192.2	34.9	0.56	2.04	2,943.1	0.8	0.3	0.6	6.0	5.3	-3.9%
336	273.2	6.1	1,187.1	36.0	0.21	2.84	2,956.4	0.8	0.6	0.9	6.0	5.5	-4.1%
476	191.4	5.7	1,214.7	37.6	DL	3.38	3,212.4	1.0	0.8	1.6	5.7	5.2	-8.7%
816	182.0	9.6	1,213.1	37.7	DL	2.98	2,893.7	1.0	0.5	1.1	6.0	5.3	-3.6%
Quench ^d at 817	184.1	5.0	1,161.6	36.1	DL	2.89	2,746.7	0.9	0.8	na	5.7	na	-3.1%
Uncertainty	±34	±5.2	±5.1	±0.3	±0.02	±0.05	±50	±0.1	±6%	na	±0.1	±0.1	na
Water chemistry (mmol/kg), supercritical CO ₂ and brine-reacted Gothic shale experiments (Gothic-CO ₂), 160°C, 15 MPa													
Initial Brine ^b	194.3	4.9	1,346.3	29.1	DL	0.93	2,956.4	0.8	0.7	na	6.7	6.1	-0.1%
28	181.5	5.7	1,305.3	32.3	0.33	1.80	3,130.0	0.9	8.9	^e	5.1	3.3	-4.5%
146	173.2	5.9	1,281.8	33.1	0.32	1.87	3,040.6	0.7	^g	^e	4.8	3.3	-4.0%
308	185.3	5.9	1,249.3	35.9	0.62	2.01	2,885.7	0.9	11.8	^e	4.9	3.3	-2.2%
477	185.5	4.6	1,234.3	34.6	0.87	2.02	2,894.0	0.8	12.0	^e	4.9	3.3	-3.0%
646	184.5	4.6	1,134.2	24.7	0.57	2.35	2,912.1	0.9	13.6	^e	5.3	3.6	-7.5%
801	180.2	5.2	1,224.2	34.9	1.73	2.20	2,879.9	0.9	4.6	^e	5.2	3.2	-3.1%
1,195	190.8	5.3	1,322.7	37.4	1.09	2.96	3,157.1	1.0	16.9	^e	5.4	3.7	-4.0%
Quench ^d at 1,197	225.1	6.3	1,631.3	43.6	1.34	1.38	3,056.3	1.1	0.5	na	5.2	na	7.9%
Uncertainty	±34	±5.2	±5.1	±0.3	±0.02	±0.05	±50	±0.1	±6%	na	±0.1	±0.1	na

^aCalculated value, see *Experimental Protocols* section for explanation of methods.

^bComposition of initial, unreacted brine.

^cAnomalously low dissolved inorganic carbon analysis contributes to lower *in situ* pH.

^dComposition of brine after experiment is terminated.

^eMeasured values were inconsistent and unreliable, values of 705.3 mmol/kg (Marine) and 656.9 mmol/kg (Gothic) were determined using the Duan *et al.* (2006) equation of state and used for *in situ* pH calculations, as explained in *Experimental Protocols* section.

^fAnalysis not available, for calculation of *in situ* pH we assumed the median value of the preceding (305 h) and subsequent (694 h) samples.

^gAnalysis not available, for calculation of *in situ* pH we assumed the same value as measured for sample at 308 h.

CO₂, carbon dioxide; DL, below detection limit; na, not applicable.

Temporal evolution of pH

The pH of the Marine-Brine experiment decreased from a value of 5.8 (24 h sample) to 5.2 (187 h sample) and, with the exception of the anomalous sample at 354 h (Table 1), remained relatively constant for the duration of the experiment (Fig. 1). In contrast, pH in the Gothic-Brine experiment and both CO₂-reacted experiments remained relatively constant (Fig. 1). The pH values of the Marine-CO₂ and Gothic-CO₂

experiments were approximately 1.5–2 pH units lower than those of the brine-reacted baseline experiments (Fig. 1), results consistent with other experimental studies of CO₂-water-rock interactions (Chopping and Kaszuba, 2012; Lo Ré *et al.*, 2014; Marcon and Kaszuba, 2015). The lower pH of the CO₂-reacted experiments was caused by dissolution of supercritical CO₂ into the brine and subsequent generation of carbonic acid. The pH in these two experiments remained relatively constant (~3.5) for the duration of each experiment.

FIG. 1. Values of *in situ* pH versus time for brine-reacted (left) and CO₂-reacted (right) experiments of Marine Tuscaloosa (filled circle) and Gothic Shale (open squares) at 160°C and 15 MPa. The pH of CO₂-reacted experiments evolves at approximately two pH units less than the pH of the brine-reacted experiments due to the dissolution of supercritical CO₂ and formation of carbonic acid in brine. Analytical uncertainties are depicted for each sample. CO₂, carbon dioxide.

This uniform pH is due to the supercritical CO₂ headspace, which functions as an infinite reservoir of CO₂ that controls the carbonic acid equilibria.

Marine Tuscaloosa experiments

Concentrations of magnesium and calcium remained relatively constant at ~6.5 and ~315 mmol/kg, respectively, for the duration of both the Marine-CO₂ and Marine-Brine experiments (Fig. 2). In contrast, concentrations of dissolved silica, iron, and sulfate exhibited important differences between the two experiments. Relative to the brine chemistry

FIG. 2. Aqueous geochemistry versus time for select analytes in brine-reacted (left) and CO₂-reacted (right) Marine Tuscaloosa experiments. For clarity, only error bars that are larger than the size of the symbol are included.

FIG. 3. Saturation index versus time for select sulfate (top), carbonate (middle), and silica (bottom) minerals in brine-reacted (left) and CO₂-reacted (right) experiments of the Marine Tuscaloosa. The horizontal line at $\log(Q/K)=0$ indicates the brine is saturated with respect to the plotted minerals. Data that plot above the line indicate the brine is supersaturated with respect to the mineral whereas data that plot below the line indicate the brine is undersaturated with respect to the mineral. Mineral abbreviations and symbols: am-SiO₂, amorphous silica (open triangles); Anh, anhydrite (closed circles); Cal, calcite (closed circles); Chal, chalcidony (closed triangles); Crs, cristobalite (open circles); Dol, dolomite (open circles); Gp, gypsum (open circles); Mgs, magnesite (open triangles); Qtz, quartz (closed circles); Trd, tridymite (open squares).

of the Marine-Brine experiment and the initial (0 h) brine composition of the Marine-CO₂ experiment, iron concentrations in the brine steadily increased throughout the duration of the 1,006 h Marine-CO₂ experiment (Table 1 and Fig. 2). Similar behavior was observed for silica, except the increase was an initial spike in concentration after 24 h of reaction, followed by a gradual attainment of a steady state concentration that was elevated by ~0.6 mmol/kg relative to that of the Marine-Brine experiment. Elevated aqueous silica is consistent with silicate dissolution and scanning electron microscopy imaging of reacted Marine-CO₂ samples reported by Mouzakis *et al.* (2016), which revealed that new pores developed on the sheet silicates. Lastly, both experiments exhibited initial spikes of aqueous sulfate concentrations after ~24 h, after which the concentrations

FIG. 4. Aqueous geochemistry versus time for select analytes in brine-reacted (*left*) and CO₂-reacted (*right*) Gothic shale experiments. For clarity, only error bars that are larger than the size of the symbol are included and potassium is not shown due to the large uncertainties relative to the concentrations (Table 1).

gradually decreased to or below initial the sulfate concentrations of ~ 2.5 mmol/kg (Fig. 2). The magnitude of the decrease was twice as much for the Marine-CO₂ experiment than that of the Marine-Brine. As described in the following paragraphs, these aqueous trends are consistent with removal from, and addition to, the brine by mineral precipitation and dissolution, respectively.

Saturation state calculations (Fig. 3) provide insight into mineral stability at experimental conditions. Throughout the duration of both experiments, the brine was saturated with respect to anhydrite and undersaturated with respect to gypsum. The Marine-Brine fluid was always supersaturated with respect to anhydrite, while the Marine-CO₂ brine started supersaturated and became saturated after 300 h. These saturation states are consistent with neoformed calcium sulfate precipitates observed by Mouzakis *et al.* (2016) and indicate that these precipitates are likely anhydrite. Those workers observed a greater extent of calcium sulfate precipitation in the Marine-CO₂ than the Marine-Brine experiment. Trends in anhydrite saturation indices, decreasing aqueous sulfate concentrations, and the relative abundance of precipitates observed are consistent with enhanced anhydrite precipitation in Marine-CO₂ compared to Marine-Brine experiments.

The brine was undersaturated with respect to the carbonate minerals calcite, dolomite, and magnesite for both Marine-CO₂ and Marine-Brine experiments (Fig. 3). The saturation indices display no coherent trend, and continuous carbonate undersaturation is the only commonality for both experiments. On average, brine in the Marine-CO₂ experiment is more undersaturated with respect to carbonates than that of the Marine-Brine baseline experiment. This relationship is consistent with the decreased pH conditions induced by

FIG. 5. Saturation index versus time for select sulfate (*top*), carbonate (*middle*), and silica (*bottom*) minerals in brine-reacted (*left*) and CO₂-reacted (*right*) Gothic shale experiments. The horizontal line at $\log(Q/K)=0$ indicates the brine is saturated with respect to the plotted minerals. Data that plot *above the line* indicate the brine is supersaturated with respect to the mineral whereas data that plot *below the line* indicate the brine is undersaturated with respect to the mineral.

dissolution of CO₂ into brine. Elevated iron concentrations in Marine-CO₂ are likely due to enhanced dissolution of iron-containing carbonates. While the iron could, in principle, also be derived from another mineral such as chlorite or pyrite, carbonate dissolution is the more likely source due to the elevated dissolution kinetics of carbonates at lower pH (Palandri and Kharaka, 2004; Kaszuba *et al.*, 2013). Additionally, the chlorite in the sandstone reservoir below the Marine Tuscaloosa was found to be a nonreactive armoring component (Lu *et al.*, 2012). Although oxidative pyrite dissolution has been observed in experiments that react rocks with CO₂ and an oxygen additive (Jung *et al.*, 2013), imaging by Mouzakis *et al.* (2016) did not reveal evidence of pyrite dissolution, likely due to the argon sparging of the initial brine. Due to the high concentrations of calcium in the initial brines and the high water to rock ratio of $\sim 54:1$ (Mouzakis *et al.*, 2016), contributions from magnesium- and calcium-releasing carbonate dissolution and juxtaposed calcium-consuming anhydrite precipitation reactions were not evident in the near-constant aqueous calcium concentration trends.

Lastly, the elevated silica concentrations in the Marine-CO₂ brine correspond to saturation indices greater than zero for quartz and other silica polymorphs, and are consistent with silicate mineral dissolution. Compared to the Marine-Brine results, the Marine-CO₂ saturation indices for quartz, chalcedony, cristobalite and tridymite, and amorphous silica experienced greater increases (Fig. 3). Saturation indices for opal proxies, cristobalite and tridymite, were calculated to provide insight into a broad range of cryptocrystalline and/or amorphous silica behavior. Silica supersaturation and inhibition of quartz precipitation in acidic, CO₂-charged fluids is consistent with previous experimental work (Kaszuba *et al.*, 2005) and field observations at CO₂ injection sites (Kaszuba and Janecky, 2009).

Gothic Shale experiments

In contrast with the Marine Tuscaloosa experiments, the brine chemistry of both Gothic Shale experiments exhibited similar behaviors in regards to aqueous sulfate concentrations and corresponding calcium sulfate saturation indices (Figs. 4 and 5). Both brines were saturated with respect to anhydrite and undersaturated with respect to gypsum. Silicate mineral dissolution did not appear to be enhanced in the Gothic-CO₂ experiment relative to the Gothic-Brine experiment. In the Gothic-Brine experiment, aqueous silica concentrations increased to a maximum of 3.4 mmol/kg after only 476 h. In contrast, it took 1,195 h of steadily increasing silica levels to reach 3.0 mmol/kg in the Gothic-CO₂ experiment. Silica concentrations in the Gothic-Brine experiment appear to have been approaching steady state values, whereas silica concentrations in the Gothic-CO₂ experiment continued to increase throughout the duration of the experiment. It is possible that silica concentrations may have continued to increase in the Gothic-CO₂ experiment given longer reaction timescales.

Iron concentrations in the Gothic-CO₂ experiment steadily increased throughout the duration of the 1,195-h experiment; no iron was measured in the initial (0 h) brine (Table 1 and Fig. 4). In contrast, aqueous iron was detected in only two samples withdrawn from the Gothic-Brine experiment (143 and 336 h). These relationships have been observed in other experimental studies of CO₂-water-rock interactions in carbonate-bearing rocks (Chopping and Kaszuba, 2012) and are consistent with dissolution of iron-bearing carbonate minerals in CO₂-charged brine relative to the control brine experiment. Despite fluctuations in the saturation states (Fig. 5), it is clear that the CO₂-charged brine was more undersaturated with respect to the carbonate minerals, which indicates enhanced carbonate dissolution in the Gothic-CO₂ experiment relative to the Gothic-Brine experiment.

Mineral precipitation

Understanding secondary phase formation is important, as it has the potential to alter caprock wetting properties and subsequent effectiveness as a seal (Chiquet *et al.*, 2007). To provide insight into potential mineral transformations, activity diagrams were developed to investigate mineral stability relationships in the system Na₂O-Al₂O₃-SiO₂-H₂O. Other than the 24-h sample (Table 1), brine in the Marine-Brine experiment is in equilibrium with albite and kaolinite and the silica activity is controlled by the solubility of quartz (Fig. 6).

FIG. 6. Mineral stability relationships for the system Na₂O-Al₂O₃-SiO₂-H₂O constructed for Marine Tuscaloosa experiments at 160°C and 15 MPa. The *dashed vertical lines* represent saturation with respect to quartz, chalcedony, proxies for opal (cristobalite and tridymite), and amorphous silica. The chemistry of the CO₂-saturated brine (Table 1) was used to construct the diagram. Activities of aqueous species for individual samples are plotted on the diagram; brine-reacted experiments are denoted by *filled symbols* and CO₂-reacted experiments in *open symbols*. Numbers in the *inset legend* indicate the hours of reaction time in the experiment (Table 1).

These relationships are consistent with the mineralogy of the Marine Tuscaloosa shale (Heath *et al.*, 2011; Mouzakis *et al.*, 2016). In contrast, brine samples from the Marine-CO₂ experiment cluster in the middle of the kaolinite stability field, indicating the potential for albite dissolution and kaolinite precipitation when the shale-brine system is exposed to supercritical CO₂ (Fig. 6). Additionally, the silica activity shifts to being controlled by the solubility of chalcedony and tridymite (opal proxy) instead of quartz. The predicted mineral stabilities for the Gothic-Brine experiment are consistent with the mineralogy of the Gothic Shale (Heath *et al.*, 2011; Mouzakis *et al.*, 2016). The fluid chemistries of the Gothic-Brine experiment indicate that albite and muscovite (illite proxy) are in equilibrium, whereas albite dissolution and muscovite precipitation are favored in the Gothic-CO₂ experiment (Fig. 7). In both Gothic Shale experiments, the controls on silica activity shift from tridymite to chalcedony and finally to cristobalite solubility (Figs. 5 and 7). The solubility of amorphous silica could ultimately control silica activity in a longer-duration Gothic-CO₂ experiment.

Potential for secondary mineral formation has implications for the evolution of porosity and permeability in shale formations. Precipitation in pores and pore throats and/or mobilization of neoformed precipitates (fines migration) derived from silicate mineral alteration and from silica-laden waters could potentially decrease the permeability of caprocks, which would be beneficial for carbon storage. In the

FIG. 7. Mineral stability relationships for the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ constructed for Gothic experiments at 160°C and 15 MPa . The dashed vertical lines represent saturation with respect to quartz, chalcedony, proxies for opal (cristobalite and tridymite), and amorphous silica. The chemistry of the CO_2 -saturated brine (Table 1) was used to construct the diagram. Activities of aqueous species for individual samples are plotted on the diagram; brine-reacted experiments are denoted by filled symbols and CO_2 -reacted experiments in open symbols. Numbers in the inset legend indicate the hours of reaction time in the experiment (Table 1).

context of hydrocarbon production in tight formations, these processes have the potential to negatively impact injectivity and reservoir transmissivity.

Mouzakis *et al.* (2016) reported newly formed, possibly sodium-bearing, aluminosilicate precipitates in reacted rock samples recovered from both brine-reacted experiments but not the CO_2 -reacted experiments. These minerals may be sodium-zeolites, potentially analcime, minerals that have not been identified in either the unreacted Gothic Shale or the unreacted Marine Tuscaloosa. Precipitation of analcime is consistent with the aqueous geochemistry of the 24-h sample of the Marine-Brine experiment (Fig. 6) and with temporal trends of the aqueous geochemistry of both brine-reacted experiments (Figs. 6 and 7). Other experimental brine+rock $\pm \text{CO}_2$ studies observed analcime precipitation only in brine-reacted experiments, as the high silica concentrations and low pH of CO_2 -saturated brine are not conducive to analcime stability (Alemu *et al.*, 2011; Lo Ré *et al.*, 2014). While analcime was observed in some CO_2 -reacted experiments (Kaszuba *et al.*, 2003, 2005), its formation in those studies is likely due to much higher initial concentrations of sodium in the brine, which promotes analcime stability.

Comparative physicochemical reactivity

Differences in the evolution of the aqueous geochemistry in the experiments suggests that the Marine Tuscaloosa was more reactive than the Gothic Shale after exposure to CO_2 -

saturated brine, which is consistent with the results of Mouzakis *et al.* (2016). Mobilization and scavenging of aqueous constituents by dissolving and precipitating minerals was pronounced in the Marine- CO_2 experiment, while differences in aqueous geochemistry between the Gothic-Brine and Gothic- CO_2 experiments were minor. The evolution of the aqueous geochemistry in these experiments is consistent with mineralogical and petrophysical changes described by Mouzakis *et al.* (2016), who observed relatively limited differences between pore network features of Gothic-Brine and Gothic- CO_2 samples. However, the specific surface area, total porosity, and unconnected porosity increased in the Marine- CO_2 sample compared to unreacted Marine Tuscaloosa and Marine-Brine samples (Mouzakis *et al.*, 2016). The agreement between the rock- and fluid-focused studies emphasizes the importance of aqueous geochemistry as an effective tracer of *in situ* processes and highlights the continued value of experimentally derived geochemical data for clarifying coupled physicochemical subsurface processes.

Conclusions

This study utilized experimentally derived aqueous geochemistry to evaluate the effects of CO_2 on brine-shale interactions for two distinct and representative CCUS caprock samples. Mineral stabilities, reaction paths, and extent of transformation were investigated. Evidence of caprock alteration includes release of iron from carbonate dissolution, supersaturation of brine with respect to quartz from silicate mineral dissolution, and precipitation of anhydrite. Differences in geochemical evolution of brine reacting with caprocks highlight the variable susceptibility of shales to reaction with CO_2 -saturated brines. Distinctive geochemical signatures that developed are consistent with mineral precipitation and pore-developing dissolution of the shales (Mouzakis *et al.*, 2016). Coupling aqueous geochemistry with mineralogical data is vital for constraining parameters that are used in reactive transport models to predict the fate and transport of CO_2 in the subsurface (Gaus *et al.*, 2005; Xu *et al.*, 2005).

We recommend that future work evaluate three additional aspects of shale reactivity. First, workers should investigate how fluid-rock ratios impact reactions, as the ratios may vary spatially and temporally in these systems, and the resultant data would be useful for parameterizing reservoir models. Secondly, reactions involving both minerals and organic matter, such as ion exchange, adsorption, and intercalation, do not conform to the simplified framework of mineral dissolution and precipitation. These reactions may obscure predicted aqueous trends and complicate interpretation of experimental data; therefore, these interactions need to be evaluated. Lastly, the potential for mineral transformations induced by interactions between water-bearing supercritical CO_2 and shale (McGrail *et al.*, 2009; Loring *et al.*, 2012; Schaefer *et al.*, 2015) requires evaluation.

Acknowledgments

Q.R.S.M. acknowledges support from the University of Wyoming School of Energy Resources and a Center for Advanced Energy Studies Graduate Assistantship award. Q.R.S.M. also acknowledges support from the U.S. Department of Energy, Office of Science, Office of Workforce

Development for Teachers and Scientists, Office of Science Graduate Student Research (SCGSR) program. The SCGSR program is administered by the Oak Ridge Institute for Science and Education for the DOE under contract number DE-AC05-06OR23100. The authors acknowledge support from an EPA Star Grant R834387 to J.M., R.J. Maxwell, A.K.N.-S., and J.K., and by a United States Department of Energy Grant DE-FE0000730 to J.M. and A.K.N.-S. J.K.'s work was also supported by the University of Wyoming School of Energy Resources. G.R. was supported as part of the Nanoscale Control of Geologic CO₂ Center, an Energy Frontier Research Center funded by the United States Department of Energy Office of Science and Office of Basic Energy Science. We acknowledge The Laboratory for Environmental and Geological Studies at the University of Colorado, particularly Fredrick G. Luiszer, for aqueous analyses. The authors also are grateful for the feedback of three anonymous reviewers, whose suggestions helped strengthen the article.

Author Disclosure Statement

No competing financial interests exist.

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