Experimental Study of Porosity Changes in Shale Caprocks Exposed to CO₂-Saturated Brines I: Evolution of Mineralogy, Pore Connectivity, Pore Size Distribution, and Surface Area

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Abstract

Carbon capture, utilization, and storage, one proposed method of reducing anthropogenic emissions of CO₂, relies on low permeability formations, such as shales, above injection formations to prevent upward migration of the injected CO₂. Porosity in caprocks evaluated for sealing capacity before injection can be altered by geochemical reactions induced by dissolution of injected CO₂ into pore fluids, impacting long-term sealing capacity. Therefore, long-term performance of CO₂ sequestration sites may be dependent on both initial distribution and connectivity of pores in caprocks, and on changes induced by geochemical reaction after injection of CO₂, which are currently poorly understood. This article presents results from an experimental study of changes to caprock porosity and pore network geometry in two caprock formations under conditions relevant to CO₂ sequestration. Pore connectivity and total porosity increased in the Gothic Shale; while total porosity increased but pore connectivity decreased in the Marine Tuscaloosa. Gothic Shale is a carbonate mudstone that contains volumetrically more carbonate minerals than Marine Tuscaloosa. Carbonate minerals dissolved to a greater extent than silicate minerals in Gothic Shale under high CO₂ conditions, leading to increased porosity at length scales < ~200 nm that contributed to increased pore connectivity. In contrast, silicate minerals dissolved to a greater extent than carbonate minerals in Marine Tuscaloosa leading to increased porosity at all length scales, and specifically an increase in the number of pores > ~1 μm. Mineral reactions also contributed to a decrease in pore connectivity, possibly as a result of precipitation in pore throats or hydration of the high percentage of clays. This study highlights the role that mineralogy of the caprock can play in geochemical response to CO₂ injection and resulting changes in sealing capacity in long-term CO₂ storage projects.

Keywords: caprock; carbon sequestration; Gothic Shale; Marine Tuscaloosa; nitrogen gas adsorption; porosity

Introduction

ELEVATED LEVELS OF anthropogenic carbon dioxide (CO₂) necessitate development of mitigation technologies such as geologic carbon capture utilization and storage (CCUS) to reduce global CO₂ emissions (IPCC, 2005). Caprocks that overlie storage reservoirs act as flow barriers to contain injected CO₂ and displaced brine to prevent CO₂ leakage into overlying shallow aquifers that can be

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detrimental to water quality (e.g., Navarre-Sitchler *et al.*, 2013b; Kirsch *et al.*, 2014). These barriers, typically shales, mudstones, or low permeability carbonates, contain small pore throats and water-wet pores that prevent the upward movement of CO₂ due to high capillary entry pressures and low permeabilities (Baines and Worden, 2004; Al-Bazali *et al.*, 2005). However, dissolution of CO₂ into pore fluids creates carbonic acid, which reduces pH and induces a state of geochemical disequilibrium. Subsequent mineral dissolution and precipitation may alter the shape, size, and number of pores, change the degree of pore connectivity, and ultimately impact caprock permeability and sealing capacity. High sealing capacity is required for geologic CCUS to be a safe long-term (hundreds to thousands of years) mitigation option (IPCC, 2005). Thus, understanding how geochemical reactions can alter caprock pore networks advances our ability to evaluate long-term caprock integrity and feasibility of geologic CCUS.

Previous researchers observed iron carbonate, illite, and smectite precipitation and calcite, quartz, illite/smectite, and chlorite dissolution when shale or mudstone caprocks were exposed to CO₂ in laboratory experiments (Kaszuba *et al.*, 2005; Andreani *et al.*, 2008; Carroll *et al.*, 2011; Lima *et al.*, 2011). Experimental work has shown that the ratio of CO₂ to H₂O in the reactive fluid can influence the composition of clay and carbonate precipitates (Kohler *et al.*, 2009). However, very little experimental data exist to make the connection between these geochemical reactions and changes in sealing capacity. In one laboratory study, porosity decreased in limestone and dolomite samples exposed to CO₂ (Tarkowski and Wdowin, 2011). It has also been demonstrated that the impact of reaction with CO₂ on caprock porosity is a function of the initial porosity and hydraulic conductivity of the samples (Labus and Bujok, 2011). Experimental work has linked geochemical reactions to characteristics of fractures that control fracture permeability in carbonate caprock; cross-sectional area and fracture surface roughness increased in carbonate core exposed to flowing fluids saturated with CO₂ (Ellis *et al.*, 2011). In this two-part study, laboratory experiments were performed to investigate the geochemical response of two caprock samples from potential CCUS sites, Gothic Shale and Marine Tuscaloosa Formation, exposed to CO₂-saturated brines, and the link between mineralogical reactions and changes to pore network structure. Here, in part I of the study, we describe the impact of geochemical reactions under experimental conditions relevant to CCUS on porosity, pore connectivity, pore size distribution, and surface area. In part II of the study (Miller *et al.*, 2016) the concomitant evolution in brine chemistry provides insight into aqueous geochemistry controls on mineral reactivity and porosity.

Methods and Materials

Caprock samples

Samples were obtained from core from the Southeast and Southwest Regional Carbon Sequestration Partnerships at Phase II CO₂ sequestration sites (Litynski *et al.*, 2008). An extensive study by Heath *et al.* (2011) provides detailed geochemical and pore network characterization of these samples outside of the work performed here. Samples of Gothic Shale were obtained from core of the Aneth Unit

H-117 well (API No. 43-037-30153) drilled in the Aneth Unit Enhanced Oil Recovery (within the Greater Aneth oil field in Utah) at 1643 m (5390') below ground surface. The Gothic Shale, a Pennsylvanian carbonate mudstone containing silt-sized quartz, calcite, dolomite, and mica in a clay matrix of illite and smectite with authigenic pyrite (Fig. 1A), is the reservoir caprock for the Aneth Unit (Chidsey *et al.*, 2009). Total carbonate mineral content in the Gothic Shale typically ranges from 20% to 30% (Hite and Lohmann, 1973; Nuccio and Condon, 1996) with percentages in the nearby Mule 31-K well from 30% to 50% carbonate (Chidsey, 2016); consistent with mineralogical observations of the Gothic Shale samples used in this study. Porosity of the Gothic Formation in the sampled core ranges from 2.7% to 4.3%, permeability ranges from 1.3×10^{-19} to 1.4×10^{-19} m², and total organic carbon (TOC) ranges from 2.2 to 4.4 weight percent (Heath *et al.*, 2011). The Gothic Shale contains type II and mixed type II–III kerogen (Heath *et al.*, 2011).

A sample of the Cretaceous Marine Shale of the Tuscaloosa Group (Fig. 1B) was taken at 2415 m (7925') below the ground surface from core collected during drilling of the Mississippi Power Company No. 1 observation well (MPC #11-1; API No. 23-059-20023). The Marine Tuscaloosa (as referred to in this article) is a potential seal for injection into basal lower Tuscaloosa Group sandstones at the Plant Daniel site in Jackson County, Mississippi. In the interval sampled, the Marine Tuscaloosa is a silica-rich mudstone containing quartz (60%), feldspar (14%), chlorite (9%), kaolinite (5%), and illite (5%), with trace calcite (5%) (Heath *et al.*, 2011). The porosity of the sampled interval is ~2.2%, permeability is $\sim 1 \times 10^{-19}$ m², and TOC is ~0.73 weight percent (Heath *et al.*, 2011). The Marine Tuscaloosa contains low maturity type II–III kerogen (Heath *et al.*, 2011).

Experimental conditions

One of the challenges encountered in the experimental study of geochemical reactions associated with CO₂ sequestration is accurately reproducing the chemical composition of formation brines. In previous experimental studies of geochemical reaction under CCUS conditions, the compositions of brines have been pure water (Busch *et al.*, 2009), NaCl brine (Lima *et al.*, 2011), and more complex brines created to establish equilibrium with minerals in the rocks (Kaszuba *et al.*, 2005; Andreani *et al.*, 2008; Ellis *et al.*, 2011). As this study was focused on understanding how geochemical reactions induced by injection of CO₂ change the physical properties of the rocks, the brine composition for each experiment was determined through a series of geochemical modeling exercises to minimize geochemical reactions associated with disequilibrium between the initial brine and minerals in the rocks. The compositions of the synthetic brines were modeled in the React module of the software Geochemists Workbench[®] (GWB) Standard 8.0 with the resident thermo.dat database (Bethke and Yeakel, 2012). For the Marine Tuscaloosa, brine chemistries reported for from three wells near the Plant Daniel Site at depth analogous to the depth of the Marine Tuscaloosa sample in the National Energy Technology Laboratory (NETL) National Brine Database (Carr *et al.*, 2009) were used as starting composition for the modeling. The NETL database at the time of study did not contain any records suitable for the

FIG. 1. Scanning electron microscope images of Gothic Shale unreacted (A–C), Gothic-Brine (D–F), and Gothic-CO₂ (G–I). Unreacted Gothic Shale is characterized by clay grains between larger framework silicate and carbonate minerals (B, C), organic carbon (*dark spots* in A), and sub-micron scale pores (C). After the control experiment pores appear at length scales $>1\ \mu\text{m}$ (D, E), Si-rich (small spherical precipitates) and Na-Al-Si containing (bundle of plated precipitates) minerals (F). After reaction with CO₂ (G–I) samples contain pores at 1–10 μm length scale (H, I) in addition to pores and dissolution features on *top* of clay grains (J). Bladed precipitates, often in bundles or rosettes (I, K), are Ca and S rich, likely anhydrite (see Miller *et al.*, 2016).

Gothic Shale sample. Therefore, a brine composition was modeled by fixing equilibrium concentrations of major chemical constituents with minerals present in the Gothic Shale at 160°C. For example, Fe²⁺, Ca²⁺, Mg²⁺, and SiO_{2(aq)} were fixed in equilibrium with the minerals pyrite, calcite, dolomite, and quartz, respectively (Table 1).

Reactions were modeled between these initial brine compositions for both samples and minerals in the rocks (Table 1) for temperature increases from the approximate *in situ* temperatures ($\sim 60^\circ\text{C}$ for Gothic Shale and $\sim 85^\circ\text{C}$ for the Marine Tuscaloosa) to an experiment temperature of up to 200°C. Based on the results from these temperature path models, an experimental temperature of 160°C was chosen and the composition of the brine at that temperature was created in the laboratory for the experiments. At 160°C the important geochemical reactions were accelerated to ensure reaction at laboratory time scales, but the geochemical reactions predicted at 160°C were the same as those predicted at the lower *in situ* temperatures. However, at temperatures $>170^\circ\text{C}$, predicted stable geochemical phases changed. This approach was successfully used in previous experimental

studies (Gunter *et al.*, 1997; Credo *et al.*, 2009; Alemu *et al.*, 2011). The modeled brine composition at 160°C was in equilibrium with all of the minerals identified in the rocks with the exception of chlorite in the Marine Tuscaloosa. It is possible that chemical variation in natural chlorite not

TABLE 1. MINERAL COMPONENTS USED TO CONSTRAIN GEOCHEMICAL MODELS OF SYNTHETIC BRINES

	<i>Gothic Shale</i>	<i>Marine Tuscaloosa Shale</i>
Mineral components ⁿ	Pyrite (Fe ²⁺) Dolomite (Mg ²⁺) Calcite (Ca ²⁺) Quartz (SiO _{2(aq)}) Maximum Microcline Smectite Illite	Chlorite (Fe ²⁺) Kaolinite Illite (Mg ²⁺) Calcite (Ca ²⁺) Quartz (SiO _{2(aq)}) K-Feldspar (K ⁺) Albite (Al ³⁺) Pyrite (SO ₄ ²⁻)

ⁿWhere a mineral phase was used to constrain composition of a given aqueous species, that species is listed in parentheses.

TABLE 2. SYNTHETIC BRINE COMPOSITION USED IN HIGH PRESSURE HIGH TEMPERATURE EXPERIMENTS

Sample	SiO ₂ (ppm)	Mg (ppm)	Mn (ppm)	Ca (ppm)	Na (ppm)	K (ppm)	Cl (ppm)	SO ₄ ²⁻ (ppm)	F (ppm)	CO ₂ (ppm)	pH ^a
Gothic Shale											
Brine	BDL	723	BDL	5 × 10 ⁴	4 × 10 ³	156	10 × 10 ⁴	5	DL	3.52	6.14
Brine + CO ₂	56	708	1.8	5 × 10 ⁴	4 × 10 ³	191	11 × 10 ⁴	77	0.7	32	6.14
Marine Tuscaloosa											
Brine	46	146	0.1	1 × 10 ⁴	6 × 10 ⁴	2650	12 × 10 ⁴	242	0.19	12	5.5
Brine + CO ₂	49	173	BDL	1 × 10 ⁴	7 × 10 ⁴	2950	14 × 10 ⁴	249	1.3	3	5.5

^aValue at experimental temperature of 160°C.

BDL, below detection limit.

represented by pure end member thermodynamic data in the geochemical modeling database contributed to the predicted disequilibrium, or that chlorite is actually out of equilibrium with the deep brines but the alteration of the chlorite is slow, that is, kinetically controlled. Laboratory grade salts were mixed with de-ionized, argon-deoxygenated water to create the synthetic Ca-Na-Cl brine for the Gothic Shale and the Na-Cl brine for the Marine Tuscaloosa (Table 2). The pH of the resulting brines was measured on filtered samples.

A series of four experiments, two each for the Gothic Shale and the Marine Tuscaloosa, were performed in 300 mL EZE-seal Hastelloy C-276 fixed volume reactors. Each shale (Table 3), its respective brine (Table 2), and supercritical CO₂ were reacted at 160°C and 15 MPa for ~45 days. A thermal sleeve was used to control temperature; pressure was controlled by injection of CO₂. Excess CO₂ was injected into the reaction chamber to ensure that the two immiscible fluid phases coexisted, and that a constant CO₂ fugacity and CO₂ saturation of the brine were maintained for the duration of the experiments (Takenouchi and Kennedy, 1964; Shyu *et al.*, 1997; Duan *et al.*, 2006). At 160°C and 15 MPa, CO₂ is a supercritical fluid that may react with the shale-brine system. In this article, we refer to these experiments as Gothic-CO₂ and Marine-CO₂. A pair of control experiments was also performed for both shales. In these experiments, referred to as Gothic-Brine and Marine-Brine, each shale and its respective brine were reacted at 160°C and 15 MPa for ~35 days. Pressure was controlled by injection of argon, a nonreactive gas, into the reaction chamber. Temperature varied by ±1.9°C in all experiments. Pressure varied by ±0.7 MPa in the CO₂-reacted experiments and ±1.9 MPa in the brine-reacted experiments. These procedures are consistent with previous investigations of supercritical carbon dioxide-

water-rock reactions (Kaszuba *et al.*, 2003, 2005; Palandri and Kharaka, 2005; Rosenbauer *et al.*, 2005; Chopping and Kaszuba, 2012).

Both rock fragments and powdered rocks were used in all experiments. Use of rock fragments promoted recovery of rocks of sufficient size that scanning electron microscopy (SEM), neutron scattering, and gas adsorption surface area analysis could be performed. Use of rock powders enhanced reactivity and maximized reaction rates. Rock fragments were 0.3–5 mm in size. Rock powders were prepared by grinding in a ceramic mortar and pestle and sieving through a 45 µm sieve. Five grams of shale (4 g of fragments and 1 g of powder) were used in all four experiments. Two hundred seventy grams of brine were used in the two CO₂-reacted experiments and 294 g of brine were used in the brine-reacted experiments, yielding initial brine/rock ratios of 54 and 58.8, respectively. The amount of CO₂ in the Gothic-CO₂ and Marine-CO₂ experiments were controlled by the dissolution of CO₂ into the brine. In the Gothic-CO₂ experiment the CO₂/rock mass ratio was 3.4 (total of 17 g of CO₂ in the brine), while in the Marine-CO₂ experiment the CO₂/rock mass ratio was 1.9 (9.5 g of CO₂ dissolved into the brine).

Brine samples were extracted during the ongoing experiments 24 h after achieving experimental conditions and subsequently at 7-day intervals. The collected samples were cooled and depressurized to ambient conditions in a few seconds and subsequently processed and analyzed as described by Miller *et al.* (2016). Measured pH values of the extracted samples were corrected to *in situ* reactor pH using Geochemist's Workbench and the b-dot ion association model (Miller *et al.*, 2016). Unreacted and reacted whole-rock samples were digested and analyzed for major cation and anion concentrations by ICP-OES (Farrell *et al.*, 1980).

TABLE 3. WHOLE ROCK CHEMISTRY IN % OXIDES

	P ₂ O ₅	MnO	Fe ₂ O ₃	MgO	SiO ₂	Al ₂ O ₃	CaO	TiO ₂	Na ₂ O	K ₂ O
Gothic Shale										
Unreacted	0.58	0.03	4.15	4.24	42.4	11.4	14.4	0.51	0.68	2.49
Brine reacted	0.45	0.02	4.03	2.97	40.8	7.95	12.2	0.49	0.38	2.45
CO ₂ reacted	0.44	0.02	3.95	3.42	44.2	11.7	14.5	0.46	0.38	2.70
Marine Tuscaloosa										
Unreacted	0.09	0.05	5.98	1.53	56.3	24.4	0.66	1.04	0.99	3.33
Brine reacted	0.10	0.01	5.46	1.52	53.5	22.5	0.65	1.01	0.58	2.95
CO ₂ reacted	0.16	0.01	4.90	1.40	60.9	23.5	0.65	0.98	0.75	3.30

Sample characterization

Small angle neutron scattering was combined with high-resolution SEM and gas adsorption surface area and porosity measurements to quantify changes in porosity and pore connectivity in nanometer to micrometer sized pores in the shales.

Small angle neutron scattering

Neutrons passing through a rock sample scatter from nanoscale objects and internal interfaces of materials if these structures (i.e., pores) possess neutron coherent scattering contrast with the bulk material (a function of the chemistry and density). The scattered intensity as a function of scattering angle contains volume averaged information about the length scales of pores within the rock and their abundance. Small-angle neutron scattering (SANS) data contain statistical information about internal surface features and structures at length scales from ~ 1 to 700 nm. Using established modeling approaches, SANS data of rock thin sections provide detailed information about the topology and architecture of nm-size pore networks (Mildner *et al.*, 1986; Radlinski *et al.*, 1999; Radlinski, 2006; Anovitz *et al.*, 2009; Jin *et al.*, 2013; Bazilevskaya *et al.*, 2014; Navarre-Sitchler *et al.*, 2013, 2015). These pore systems are often highly disordered and scale invariant, and can be mathematically described by fractal and polydisperse hard-sphere models, which provide information about the pore size distribution, pore volume, and surface roughness and area (Hinde, 2004; Radlinski, 2006).

Samples of unreacted, CO₂-reacted, and brine-reacted Gothic Shale and Marine Tuscaloosa formation were broken in chips <1 mm and packed into quartz cuvettes with 1-mm path length for SANS analysis. SANS data were collected at the High Flux Isotope Reactor (HFIR) facility at Oak Ridge National Laboratory (ORNL) on the General Purpose SANS (CG-2) and Bio SANS (CG-3) beamlines. Data of scattering intensity versus momentum transfer (Q) were taken over a Q range from 0.0008 to 0.86/Å on CG-2 and from 0.0012 to 0.40/Å on CG-3. The raw data were reduced and processed using standard data reduction practices, including background and empty cell correction (a blocked beam and an empty cuvette), background scattering correction, transmission normalized, radially averaged, and normalized to absolute intensities (Kline, 2006, DeBeer-Schmitt and Bailey,

2011). Although shale samples cut perpendicular to the bedding plane often yield asymmetric 2D scattering patterns (Hall and Mildner, 1983; Gu *et al.*, 2015), the random packing of shale chips in the cuvette produced azimuthally symmetric 2D scattering, averaging out asymmetries in the pore shapes. The scattering data were fit to Equation (1) to determine the constant c , which represents the incoherent.

$$I(Q) = bQ^{-m} + c, \quad (1)$$

scattering background attributed primarily to hydrogen in the sample. This incoherent scattering was subtracted from the data because it contains no structural information.

The slope m on a log-log plot of the data captures the fractal nature of the scattering. Scattering intensity ($I(Q)$) is proportional to the square of the difference in scattering length densities ($\Delta\rho_j^*$) between solid phases (minerals and kerogens) and pores (two phase approximation). The coherent scattering length density ρ_j^* for a solid phase is given by Equation (2) (www.ncnr.nist.gov/resources/sldcalc.html):

$$\rho_j^* = \frac{\sum_{i=1}^n b_{ci}}{V_m}. \quad (2)$$

Here, b_{ci} is the bound coherent scattering length of atom i , summed up over all n atoms of a substance, and V_m is the molecular volume (g/mol). The values of the scattering length densities (ρ_j^* , Å⁻²) were calculated for each shale from bulk chemical formulas and range from 4.36×10^{-6} to 4.57×10^{-6} Å⁻² (Table 4). Rarely is the chemical composition of kerogen measured. Rather the type of kerogen is determined from the Hydrogen Index (HI) and Oxygen Index (OI). ρ_j^* for type II–III kerogens ranges from 3.4×10^{-6} Å⁻² for kerogen composition of H/C=0.5 and O/C=0.3 with density of 1.5/g/cm³ to 1.4×10^{-6} Å⁻² for compositions of H/C=1 and O/C=0.1 and density of 1 g/cm³. These kerogen ρ_j^* values are similar to calculated ρ_j^* values of the shale samples without organics (Table 4). Although an additional term in the scattering may arise from scattering contrast between the minerals and kerogen, this contrast is here small compared to the large scattering contrast of mineral–pore or kerogen–pore interfaces (with ρ_j^* of pores being 0). Therefore, pore–mineral and pore–kerogen interfaces scatter with significantly

TABLE 4. RESULTS FROM SMALL-ANGLE NEUTRON SCATTERING AND BET ANALYSIS

	Grain density, (g/cm ³)	SLD ^c (E10), (/cm ²)	Median pore diameter (nm) ^a	Median pore diameter (nm) ^b	Total surface area ^a (m ² /g)	Connected surface area ^a (m ² /g)	Connected surface area ^b (m ² /g)	Total porosity (%)	Connected porosity ^a (%)	Connected porosity ^b (%)
Gothic Shale										
Unreacted	3.06	4.42	1.6	23.1	70.3	30.1	2.3	4.21	1.53	3.71
Brine Reacted	3.01	4.39	2	26.1	80.2	37.6	1.96	5.64	2.55	4.32
CO ₂ reacted	3.04	4.36	1.3	15.7	91.3	44.3	4.05	5.54	2.09	4.98
Marine Tuscaloosa Shale										
Unreacted	3.06	4.57	1.3	8.9	53.6	41.9	14.6	3.22	1.10	8.79
Brine Reacted	3.06	4.53	1.6	4.9	49.3	14.7	31.95	3.16	2.18	10.6
CO ₂ reacted	3.02	4.57	1.3	4.9	63.2	39.6	34.13	3.75	0.65	11.4

^aDetermined from small-angle neutron scattering data.

^bDetermined from BET N₂ gas adsorption data.

BET, Brunauer Emmett Taylor.

higher intensity than mineral–mineral and mineral–kerogen interfaces, and the scattering data may be interpreted using the two-phase approximation (e.g., Kahle *et al.*, 2004; Radlinski, 2006; Anovitz *et al.*, 2009). $I(Q)$ was fit to a polydisperse hard sphere model using the two-phase approximation and fitting routines implemented in the program PRINSAS (Hinde, 2004). From this model, the size and surface area distributions of nanopores and a histogram of pore sizes were calculated.

Samples were soaked with a 75% D₂O–H₂O mixture with similar scattering contrast as the rock ($3.39 \times 10^{-6} \text{ \AA}^{-2}$) and reanalyzed to assess connected (water-accessible) porosity versus unconnected porosity. Samples were equilibrated with contrast-matched fluid for ≥ 72 h. Connected porosity was determined by difference between the scattering data from the dry samples and the contrast-matched samples.

Scanning electron microscopy

High-resolution images of unreacted and reacted samples were collected using a JEOL Ltd. JSM-7000F field emission scanning electron microscope (FESEM) with EDAX Genesis Energy Dispersive X-Ray (EDAX) Spectrometer at Colorado School of Mines to collect energy dispersive spectra (EDS). The shale chips were mounted on JEOL Ltd. JSM-840 12.5 mm diameter, 10 mm tall aluminum stubs with liquid carbon dag and vacuum sputter gold coated to reduce charging of the surface. Electron backscatter images were collected using a TSL Electron Backscatter Diffraction Detector. Approximately 400 images were collected using an accelerating voltage ranging from 5 to 10 kV.

Gas adsorption

Surface area and porosity were measured with N₂ gas on unreacted and reacted samples using Brunauer Emmett Taylor (BET) analysis. Isotherms were measured over a relative pressure range from 3×10^{-5} to 1 using ~ 1 g of sample and a Micromeritics ASAP 2020 surface area analyzer. To enable BET measurement, the samples were ground to particles of diameter ranging from 0.125 to 0.25 mm. A modification of the BET method was used on the Gothic Shale sample due to the high component of pores < 2 nm detected in the isotherms (Rouquerol *et al.*, 2007).

Results and Discussion

Changes in pore morphology

Gothic Shale is composed of clay minerals that fill spaces between larger grains of silicate framework and carbonate minerals mixed with organic matter (Fig. 1A, B). At micrometer length scales $< 10 \mu\text{m}$, intergranular pores parallel to clay sheets (Fig. 1B) and 100 nm to $5 \mu\text{m}$ length scale pores between grains and clay sheets are observed in SEM images (Fig. 1C). Pores $< 1 \mu\text{m}$ in length scale appear to associate with organic material throughout unreacted Gothic Shale samples. While precise measurement of pore length scales at resolution < 10 nm was not feasible with the FESEM, qualitatively the Gothic Shale contains numerous < 10 nm length scale intergranular and intragranular pores and roughness of mineral surfaces at the same length scale. SEM images of unreacted Gothic Shale are consistent with a low permeability caprock with pores at length scales ranging from

< 10 nm to $10 \mu\text{m}$, and most of the porosity in pores of sub-micron sizes (Fig. 1A–C).

Compositions of the fluids extracted from the Gothic–CO₂ experiment vessel are consistent with CO₂ dissolution into the brine (decrease in pH by 1.5–2 U below control experiments, ~ 5.5 compared to ~ 3.5), and subsequent mineral dissolution (Miller *et al.*, 2016). pH in the brine-reacted experiment is higher than in the CO₂-reacted experiment providing less chemical drive for mineralogical reactions. High-resolution images of the CO₂-reacted and brine-reacted Gothic Shale samples show evidence of geochemical reactions, Fe concentrations in the brines are consistent with dissolution of iron-bearing carbonates in the sample (Miller *et al.*, 2016). Brine-reacted samples contain silicon-rich precipitates (analyzed with EDS) from ~ 50 nm spheres to 400 nm plate bundles that are not present in the CO₂-reacted samples (Fig. 1F), consistent with silicate mineral dissolution and silica stability (Miller *et al.*, 2016). Precipitates comprised of Na, Al, and Si also were observed as bundles of platy precipitates (Fig. 1F), and are consistent with analcime stability in the control experiments (Miller *et al.*, 2016). In general, small slit-shaped pores ($< 10 \mu\text{m}$) in the unreacted samples grew in diameter during the Gothic–Brine experiment (Fig. 1E) and pores $> 10 \mu\text{m}$ appear in the Gothic–Brine samples as well (Fig. 1D). At length scales > 10 nm, the Gothic–CO₂ does not appear much different from the unreacted Gothic Shale (Fig. 1A, G). However, the small slit-shaped pores appear larger in SEM images ($< 1 \mu\text{m}$ in unreacted compared to $> 1 \mu\text{m}$ in the reacted samples) and new pores were created at length scales $< 10 \mu\text{m}$ (Fig. 1H). Enlarged intergranular pores parallel to and surrounded by clay sheets are abundant in the Gothic–CO₂ (Fig. 1H) and there appear to be more intergranular nanopores (> 100 nm) between grain boundaries and more precipitates relative to the unreacted samples (Fig. 1K). Clay mineral surfaces in the CO₂-reacted samples exhibit pores ~ 10 nm to $1 \mu\text{m}$ in size that are not present in the unreacted or brine-reacted samples (Fig. 1J). Gothic–CO₂ samples contain calcium sulfate precipitates with bladed or rosette morphology that are as large as $80 \mu\text{m}$ (Fig. 1I) and are likely anhydrite (see Miller *et al.*, 2016).

Pores at length scales $> 10 \mu\text{m}$ are not apparent in samples of unreacted Marine Tuscaloosa (Fig. 2A). Slit-shaped pores are found at length scales from 100 nm to $10 \mu\text{m}$ (Fig. 2B, C), and appear to occur predominantly between grains of clay minerals, with very few intragranular pores (Fig. 2C). Like in the Gothic Shale experiments, CO₂ injection reduced the pH by ~ 2 pH units (from 5.5 to 3.5). No decrease in pH was observed with injection of argon gas in the brine-reacted experiments. Also like in the Gothic Shale samples, both Marine–CO₂ and Marine–Brine samples show evidence of geochemical reactions. Marine–Brine samples contain new SiO₂-rich, platy precipitates similar to the ones in the Gothic–Brine samples (Fig. 2F, small blade-shaped precipitates), and consistent with Si activity control by solubility of silica precipitates (Miller *et al.*, 2016). There is little visual evidence for mineral dissolution in the Marine–Brine samples (Fig. 2D–F). In contrast, slit-shaped pores at ~ 100 nm length scales in the Marine–CO₂ appear to increase in size (Fig. 2H) and new intragranular pores appear on the surfaces of minerals (not shown), consistent with silicate mineral dissolution indicated in geochemical analysis of the

FIG. 2. Scanning electron microscope images of unreacted Marine Tuscaloosa (A–C), Marine-Brine (D–E), and Marine- CO_2 (G–I) samples. Porosity in the unreacted Marine Tuscaloosa is characterized mostly by pores between clay grains at $<1\ \mu\text{m}$ length scale (C), with little visible porosity at length scales $>10\ \mu\text{m}$ (A, B). Samples from the control experiments also do not contain many pores at length scales $>1\ \mu\text{m}$ (D, E), but pores $<1\ \mu\text{m}$ appear to increase in number (F) and small Si-rich bladed precipitates occur on the surfaces of the samples (F). Marine- CO_2 samples, in contrast, contain pores at length scales $>10\ \mu\text{m}$ and numerous bladed precipitates (I) of Ca-S composition (likely anhydrite, see Miller *et al.*, 2016). Clay minerals appear hydrated and altered at length scales $<1\ \mu\text{m}$ (J).

brine (Miller *et al.*, 2016). SEM images also show evidence of hydration and/or dissolution of clay minerals (Fig. 2J), which was not observed in the Gothic- CO_2 samples. Bladed calcium sulfate precipitates are found in the Marine- CO_2 (Fig. 2I), but are smaller and fewer than in the Gothic- CO_2 samples. In summary, both Gothic- CO_2 and Marine- CO_2 samples show evidence of mineral dissolution, increases in pore size, and creation of new pores while brine-reacted samples show less evidence of mineral reaction and new pore creation, and precipitates are silica rich. Evidence of mineral dissolution is more abundant in SEM images of the Marine- CO_2 compared to the Gothic- CO_2 samples, consistent with element release and aqueous chemistry of the brines (see Miller *et al.*, 2016).

Changes in porosity, pore connectivity, and surface area

FESEM images provide qualitative evidence of mineral dissolution, mineral precipitation, and increased porosity in the CO_2 -reacted samples of Gothic Shale and Marine Tuscaloosa.

Observationally, the results are consistent with experimental results of Labus and Bujok (2011). Small-angle neutron scattering and gas adsorption (BET) data provide quantitative evidence of changes to porosity, pore connectivity, and other important physical aspects of the pore networks. SANS interrogates the internal structure of rock providing information regarding changes to pore structure that is inaccessible through imaging alone.

In unreacted samples of Gothic Shale and Marine Tuscaloosa pores $<10\text{ nm}$ in length scale dominate the pore size distribution calculated from neutron scattering data (Fig. 4). The BET data from the Marine Tuscaloosa sample show a similar dominant pore size of $<5\text{ nm}$. BET data from the Gothic Shale samples are inconclusive, presumably due to the high number of angstrom to nm scale pores and high organic carbon content that can be problematic for N_2 BET analysis (Sing *et al.*, 1982).

Total and connected porosity in the unreacted Gothic Shale calculated from SANS data are 4.2% and 1.5%, respectively (Fig. 3B). Porosity increased in the Gothic-Brine samples relative to the unreacted Gothic Shale in both the connected

FIG. 3. Connected and unconnected pore volume for unreacted samples of Marine Tuscaloosa and Gothic Shale compared to samples from the control and CO₂ experiments.

and unconnected portions of the pore network (Table 4 and Fig. 3B). Interestingly, the total porosity in the CO₂-reacted samples is the same as in the brine-reacted sample, consistent with similar features observed in SEM images of the Gothic-Brine and Gothic-CO₂ samples. However, the connected porosity is lower in the Gothic-CO₂, consistent with decreased connected porosity in CO₂-reacted carbonate rocks reported by Tarkowski and Wdowin (2011). The resulting changes in total and connected porosity are attributed to a combination of a greater degree of mineral dissolution at length scales <1 mm (Fig. 1H), and concomitant precipitation that blocks porosity (Fig. 1I). The combination of simultaneous mineral dissolution and precipitation reactions results in little change in total porosity but decreased connected porosity in the Gothic-CO₂. The pore sizes that contribute to the changes in porosity are different in the Gothic-Brine and Gothic-CO₂ samples. In the Gothic-Brine, porosity in pores <100 nm diameter did not increase relative to the unreacted Gothic Shale (Fig. 1A). In contrast, in the Gothic-CO₂ sample porosity increased at all length scales compared to the unreacted Gothic Shale, and the increase in porosity at length scales >300 nm in the Gothic-CO₂ is the same as in the Gothic-Brine (Fig. 4B). Thus, while the total porosity would suggest that the CO₂-reacted experiment produced the same results as the brine-reacted sample, the pore size distribution data show important differences in how that porosity was generated.

Increase in porosity in the Gothic Shale samples is accompanied by an increase in specific surface area from 70.3 m²/g (43% connected) in unreacted samples to 80.2 m²/g

(47% connected) in the Gothic-Brine samples, and 91.3 m²/g (49% connected) in Gothic-CO₂ samples. Most of the surface area increase is attributed to connected pores that are 14–200 nm in diameter. Median pore size increases from 1.6 nm in the unreacted samples to 2 nm in Gothic-Brine samples and 1.3 nm in the Gothic-CO₂ samples. Again, due to the difficulty of BET analysis on the Gothic Shale samples, the BET surface area (<5 m²/g) was significantly less than surface area calculated from SANS data, and is likely erroneous.

Unlike in the Gothic Shale samples, the Marine-CO₂ total porosity is higher than both the unreacted Marine and Marine-Brine total porosities (Fig. 3). The SANS calculated porosities of the unreacted Marine Tuscaloosa and Marine-Brine samples are 3.2%, which increased to 3.8% in the Marine-CO₂ samples (Fig. 3). Interestingly, the connected porosity in the brine-reacted samples is higher (2.2%) than both the unreacted (1.1%) and CO₂-reacted (0.7%) samples, and the connected porosity is lowest in the CO₂-reacted samples. Pores with <10 nm diameter dominate in all samples (Fig. 4A). Neutron scattering showed that porosity increased in both the Marine-CO₂ and Marine-Brine samples at nearly all pore sizes, with greater increases in Marine-CO₂ compared to the Marine-Brine samples (Fig. 4A). In general, there appears to be no preferential pore size subjected to either dissolution or precipitation in the Marine Tuscaloosa samples. Decrease in connected porosity in the Marine-CO₂ may be related to the hydration and alteration of clay minerals at length scales <100 nm observed in SEM images (Fig. 2J). The clay content of the Marine Tuscaloosa (19% clay, 5% calcite) is higher than that of the carbonate-rich

FIG. 4. Cumulative porosity for Gothic (A) and Marine Tuscaloosa (B) shale samples calculated from SANS data. Total porosity in the Gothic-Brine and Gothic- CO_2 samples is approximately the same and 1.5% higher than the Gothic unreacted samples. In the Gothic-Brine experiments much of the increased porosity occurred in pores >200 nm diameter. In contrast, in the Gothic- CO_2 experiment the increased porosity is attributed to smaller pores, <300 nm diameter. Marine-Brine and Marine- CO_2 samples have higher porosity than the unreacted Marine Tuscaloosa sample and porosity is created at all length scales analyzed by SANS (1–500 nm pore diameter).

Gothic Shale ($\sim 12\%$ clay, $\sim 45\%$ carbonate average in Gothic Shale near the sample well, data from Chidsey (2016). These differences in mineralogy possibly explain the difference in connected porosities of these two samples after reaction with CO_2 . Surface area is lower in the Marine-Brine samples ($49.3 \text{ m}^2/\text{g}$, 70% in connected pores), but higher in the Marine- CO_2 samples ($63.2 \text{ m}^2/\text{g}$, 63% in connected pores) as compared to the unreacted samples ($53.6 \text{ m}^2/\text{g}$, 78% in connected pores). In both the Gothic- CO_2 and Marine- CO_2 samples, the median pore diameter is slightly higher (~ 4 nm) compared to corresponding unreacted samples (~ 3 nm). While we didn't perform permeability tests on the reacted samples due to the small sample sizes, an increase in pore size and porosity can correspond to an increase in permeability. However, the surface area also increases in both CO_2 -reacted samples, which can contribute to decreases in permeability. Therefore, predictions regarding the changes in permeability of these samples are not possible with the current data.

Conclusions

Samples of caprocks from two different CO_2 sequestration pilot projects were experimentally evaluated for evidence of mineral dissolution and precipitation and related changes in porosity, pore connectivity, and surface area as a result of geochemical reaction under simulated CO_2 sequestration conditions. Results from the CO_2 -reacted samples were compared to results from a set of control experiments where argon, not CO_2 , was used to maintain a pressure of 15 MPa in the autoclave reactor with brine and shale samples. Results from these experiments demonstrate that both the Gothic Shale and Marine Tuscaloosa experience mineral dissolution under CO_2 sequestration conditions, and in both sets of experiments more extensive mineral reactions were observed in the CO_2 experiments compared to the control experiments. In Brine-experiments silica-rich bladed and/or spherical-shaped

mineral precipitates were observed in SEM images compared to Ca-sulfate precipitates in both the Gothic- CO_2 and Marine- CO_2 experiments. In the Gothic Shale, both total porosity and connected porosity increased under reactive conditions relevant to CO_2 sequestration. In the Marine Tuscaloosa, total porosity increased slightly but connected porosity decreased. Despite larger increases in total nanoscale porosity (as measured by SANS) in the Gothic- CO_2 compared to the Marine- CO_2 samples, overall the Marine- CO_2 samples appear the most reacted in SEM images with increased abundance of pores $>1 \mu\text{m}$. Differences in aqueous geochemistry between the two experiments are also consistent with more reactive Marine Tuscaloosa compared to the Gothic Shale (Miller *et al.*, 2016).

Total porosity, pore connectivity, and surface area increased in both the brine-reacted and CO_2 -reacted samples Gothic Shale. In contrast, total porosity did not change but connected porosity increased in the brine-reacted Marine Tuscaloosa samples, while the total porosity increased and connected porosity decreased in the CO_2 -reacted Marine Tuscaloosa samples. SEM images of the Gothic Shale and Marine Tuscaloosa CO_2 -reacted samples exhibited increased numbers and sizes of pores, consistent with data from small angle neutron scattering and BET analyses. SEM observations of increased numbers of large pores, combined with increased mobilization of solutes and aqueous geochemical evidence presented in Miller *et al.* (2016) suggest that the Marine Tuscaloosa caprock may be more susceptible to long-term loss of sealing capacity with geochemical reaction compared to the carbonate-rich Gothic Shale. However, neutron scattering analysis demonstrates a decrease in connected porosity in small pores, likely due to precipitation or clay hydration, which may limit the connectivity of any enhanced porosity. It is unclear from SEM images if the increased porosity at larger length scales is connected or unconnected. Dissolution of silicate minerals in the higher

pH brine-reacted experiments appeared to result in the formation of silicate precipitates not observed in the CO₂ experiments. General agreement between rock and fluid chemistry in these experiments point to aqueous geochemistry as a potentially important source of information about downhole coupled physicochemical processes.

We recommend future research to evaluate porosity changes in intact rock core under *in situ* lithostatic pressure conditions. These more complicated experiments will shed light on heterogeneous development of pores related to heterogeneity in fluid flow paths through the rock and spatial and temporal evolution of geochemical reactions along fluid flow paths.

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